

## PATENT ABSTRACTS OF JAPAN

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**(54) ELECTROSTATIC CHARGE IMAGE DEVELOPING TONER AND METHOD FOR MANUFACTURING THE SAME****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide an electrostatic charge image developing toner which is low in fixing temperature, is capable of dealing with energy saving, high speed of printing and copying and coloring, has an excellent preservable property and flowability, is high in offset temperature, does not generate smells and is capable of forming good-quality images with high resolution.

**SOLUTION:** The electrostatic charge image developing toner which contains at least a binder resin and colored polymer particles containing coloring agents and in which the binder resin is a polymer bonded with 7-20C alkylthio group having a structure, which has at least two ternary carbon atoms and in which a sulfur atom is directly bonded to at least one ternary carbon atom among these atoms and the method for manufacturing the same.

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**CLAIMS**

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[Claim(s)]

[Claim 1]In a toner for electrostatic charge image development containing a colored polymer particle which contains binding resin and colorant at least, A toner for electrostatic charge image development being the polymer which an alkylthio group with 7-20 carbon atoms in which this binding resin has the structure which has at least two tertiary carbon atoms, and a sulfur atom coupled directly with at least one of tertiary carbon atoms of it combined.

[Claim 2]The toner for electrostatic charge image development according to claim 1 whose outflow starting point (Tfb) softening temperature (Ts) of a toner measured with a flow tester is not less than 110 \*\* at 62-67 \*\*.

[Claim 3]In a manufacturing method of a toner for electrostatic charge image development including a process which carries out suspension polymerization of the monomeric mixture which contains a polymerization nature monomer and colorant at least, and makes a colored polymer particle generate in a drainage system carrier fluid body containing dispersion stabilizer, In this monomeric mixture, it has at least two tertiary carbon atoms as a chain transfer agent, And a manufacturing method of a toner for electrostatic charge image development making the third class thiol with 7-20 carbon atoms which have the structure which a sulfur atom coupled directly in at least one of tertiary carbon atoms of it contain.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]**This invention relates to a toner for electrostatic charge image development used for the development of the electrostatic latent image formed in a xerography, an electrostatic recording method, an electrostatic printing method, etc., and a manufacturing method for the same.

**[0002]**

**[Description of the Prior Art]**In a xerography, an electrostatic recording method, an electrostatic printing method, etc., the toner (toner for electrostatic charge image development) is used as a developer for visualizing the electrostatic latent image formed on the photo conductor. A toner is a coloring particle containing binding resin, colorant, a charge controlling agent, a release agent, etc. The manufacturing method of a toner is divided roughly into pulverizing method and the polymerizing method. Pulverizing method is a method of carrying out melt kneading, ranking second, grinding and classifying each ingredient, such as binding resin and colorant, and manufacturing a toner (pulverizing method toner). In pulverizing method, since it is necessary to use the thing of construction material with the brittleness which is easy to be ground as binding resin, it is generated by a lot of impalpable powder according to a grinding process. Although a classification must remove such impalpable powder, a process is complicated and, moreover, the yield becomes low. Since a pulverizing method toner is construction material with weak binding resin, pulverization is carried out within devices, such as a copying machine, at the time of use, and, as a result, image quality deteriorates.

**[0003]**On the other hand, the polymerizing method is a method of making the polymer particle containing colorant etc. generating, by carrying out suspension polymerization of the monomeric mixture which contains a polymerization nature monomer, colorant, a charge controlling agent, a release agent, etc. in the drainage system carrier fluid body containing dispersion stabilizer. In the polymerizing method, the obtained colored polymer particle can be used as a toner (polymerization toner). thus, the polymerizing method — if — since a grinding process is not needed, the material which can form the polymer which is hard to be ground as a polymerization nature monomer can be chosen. since polymerization toner is a globular form substantially, it is excellent in mobility, and, moreover, particle size distribution boils it markedly as compared with a pulverizing method toner, and it is sharp.

**[0004]**It is minute to the toner for electrostatic charge image development, the picture of the outstanding high-concentration image quality can be formed in it, and image quality does not deteriorate in it by change of environment, such as temperature and humidity, either, but, moreover, it is required for it are continuous printing, that a consecutive copy should be possible, etc. In addition to these characteristics, the toner for electrostatic charge image development is urged for it to be able to respond to improvement in the speed of that it can contribute to energy saving, printing, and a copy, to be able to respond to full color-ization, etc. these days. Therefore, moreover, in addition, the toner for electrostatic charge image development is urged to improve fixability, such as a fall of fixing temperature, without maintaining high definition and spoiling preservability.

[0005]Specifically in image forming devices with which the toner for electrostatic charge image development is used, such as a copying machine of an electrophotographing system, and a printer, reduction of power consumption is attained these days. The process of consuming energy also especially in an electrophotographing system is a fixing process for being established, after transferring the toner image on a photo conductor on transfer materials, such as paper. Generally, in the fixing process, in order to fix a toner image on a transfer material, the fixing roll and fixing belts which were heated at not less than 150 \*\* are used, and the electrical and electric equipment is used as the energy source. Lowering this fixing temperature is called for from a viewpoint of energy saving.

[0006]Improvement in the speed of printing speed or copy speed is called for these days. While composite-izing of an image forming device and the network of a personal computer progress especially, the demand to high speed printing or high speed copying is increasingly stronger. Therefore, in the high speed printer or the high speed copying machine, shortening of fixing time is needed.

[0007]In the design of the toner for electrostatic charge image development, there is a method of reducing the glass transition temperature (Tg) of binding resin as the technique of meeting the demand from such an image forming device. However, if Tg of binding resin is reduced, all over preservation of a toner, or the toner box of a developer, particle toner will cause blocking mutually, and will be floc, and it will be a toner what is called with bad preservability.

[0008]These days, the color printing and color copying art by an electrophotographing system are developed. In order to perform color printing and color copying, usually the electrostatic latent image on a photo conductor was developed using the color toner of 3 thru/or 4 colors, and was transferred at once or one by one on the transfer material, and it is established after an appropriate time. For this reason, the thickness of the toner established compared with a monochrome image becomes thick. In order to make it color to a predetermined color tone with mixed colors, it is required at the time of fixing to carry out melting of two or more overlapping color toner uniformly.

[0009]Therefore, it is necessary to make it easy to design the melt viscosity near fixing temperature low compared with the conventional thing, and to fuse in color toner. There are methods, such as making the molecular weight of binding resin low, or lowering Tg as the technique of making melt viscosity of a toner low, compared with the conventional toner. However, by any method, it will be easy to cause blocking and will be a toner with bad preservability. Thus, adoption of the refining technique of the toner corresponding to energy saving, improvement in the speed of printing or a copy, and colorization will reduce the preservability of a toner.

[0010]Conventionally, the fixing temperature of the toner for electrostatic charge image development is lowered, and the toner which has core shell structure is simultaneously proposed as the technique of raising blocking resistance. It is the method of forming the particle toner (it is also called capsule toner) of the structure which specifically used as the core the coloring particle which contains binding resin and colorant at least and in which Tg covered this core with high resin. In the polymerizing method, carry out suspension polymerization of the polymerization nature monomeric mixture which contains a polymerization nature monomer and colorant at least, make a colored polymer particle generate, and it ranks second, The method of making the polymer particle of core shell structure generate is known by polymerizing the polymerization nature monomer which can generate the polymer of Tg higher than Tg of the polymer component which constitutes this colored polymer particle under existence of this colored polymer particle. If this technique is adopted, the polymer particle of the structure which covered the circumference of the colored polymer particle (core) of low Tg with the thin polymer layer (shell) of high Tg can be obtained.

[0011]The toner of such core shell structure can control blocking of toners by the shell which consists of a polymer layer of high Tg while being able to lower fixing temperature by making low enough Tg of the binding resin which constitutes a core. However, since the temperature which offset generates would also become low if Tg of the binding resin which constitutes a core is lowered in order to lower fixing temperature even if it is a toner of such core shell structure, it

was difficult to obtain high definition.

[0012]In order to adjust the molecular weight of binding resin conventionally, the method of polymerizing a polymerization nature monomer under existence of chain transfer agents, such as t-dodecyl mercaptan, is known (for example, paragraph number [0032] of JP,11-38674,A). When binding resin is manufactured using a chain transfer agent, \*\* which makes the molecular weight of binding resin low is made, and since the reduction in Tg is also easy, improvement in the melting characteristic of a toner and reduction of fixing temperature are expected.

[0013]However, in order that mercaptans proposed as a typical chain transfer agent by the technical field of the toner from the former, such as t-dodecyl mercaptan and n-dodecyl mercaptan, might remain in binding resin, there was a problem that a toner generated a pungent smell. If the amount of these mercaptans used is lessened, fixing temperature of a toner of what can control the bad smell of a toner cannot fully be lowered. On the other hand, if the amount of these mercaptans used is increased, in addition to the pungent smell of what can fully lower the fixing temperature of a toner becoming strong, offset generating temperature will also become remarkably low and the blocking resistance of a toner will also fall remarkably further. Such a tendency is the same also in the toner of core shell structure. Therefore, it was difficult actually to obtain the toner with which these mercaptans are used for molecular weight adjustment, and it can be satisfied of mercaptans in respect of reduction of the melting characteristic or fixing temperature, preservability (blocking resistance), mobility, etc.

[0014]

[Problem(s) to be Solved by the Invention]The purpose of this invention has low fixing temperature, and Energy saving, printing, and improvement in the speed of a copy, It can respond to colorization etc. and, moreover, in addition, excels in preservability and mobility, and offset temperature is high, there is also no generating of a bad smell, and it is in providing the toner for [ which can form the picture of good image quality with high resolution ] electrostatic charge image development, and its manufacturing method.

[0015]This invention persons found out that said purpose could be attained with the toner containing the binding resin obtained as a chain transfer agent using the third class thiol which has a structure specific at the time of a polymerization, as a result of inquiring wholeheartedly. Namely, it has at least two tertiary carbon atoms as a chain transfer agent at the time of the polymerization of binding resin, And if the third class thiol with 7-20 carbon atoms which have the structure which the sulfur atom coupled directly in at least one of tertiary carbon atoms of it is used, Comparatively little use can also fully lower the fixing temperature of a toner, and moreover can maintain offset generating temperature highly, a bad smell does not have it, either, further, it can excel in preservability and mobility and the toner for electrostatic charge image development which forms good image quality with high resolution can be obtained.

[0016]Conventionally, the third class thiol which has this specific structure is a technical field of a toner, and is the compound which was not used as a chain transfer agent or a regulator. In order that the third class thiol may participate in a chain transfer reaction, at least a part of the third class thiol used at the time of a polymerization will be combined as an alkylthio group in the generated polymer (binding resin) after a polymerization. This invention comes to be completed based on these knowledge.

[0017]

[Means for Solving the Problem]In a toner for electrostatic charge image development which contains a colored polymer particle which contains binding resin and colorant at least according to this invention, A toner for electrostatic charge image development being the polymer which an alkylthio group with 7-20 carbon atoms in which this binding resin has the structure which has at least two tertiary carbon atoms, and a sulfur atom coupled directly with at least one of tertiary carbon atoms of it combined is provided.

[0018]According to this invention, in a manufacturing method of a toner for electrostatic charge image development including a process which carries out suspension polymerization of the monomeric mixture which contains a polymerization nature monomer and colorant at least, and makes a colored polymer particle generate in a drainage system carrier fluid body containing dispersion stabilizer, in this monomeric mixture as a chain transfer agent, A manufacturing

method of a toner for electrostatic charge image development making the third class thiol with 7–20 carbon atoms with structure which has at least two tertiary carbon atoms, and a sulfur atom coupled directly with at least one of tertiary carbon atoms of it contain is provided.

[0019]

[Embodiment of the Invention]1. Although the manufacturing method in particular of the toner for electrostatic charge image development of manufacturing method this invention of the toner for electrostatic charge image development is not limited, it is preferred to adopt the polymerizing method. The polymerization toner by the polymerizing method can usually be obtained as a polymer particle (colored polymer particle) containing colorant etc. in the drainage system carrier fluid body containing dispersion stabilizer by carrying out suspension polymerization of the monomeric mixture which contains a polymerization nature monomer and colorant at least. . Make a monomeric mixture contain the third class thiol specific as a chain transfer agent in this invention in addition to a polymerization nature monomer and colorant. A cross-linking monomer, a charge controlling agent, a release agent, other regulators, a macro monomer, a polymerization initiator, and other various additive agents can be made to contain if needed.

[0020]The polymerization toner of core shell structure in the drainage system carrier fluid body containing dispersion stabilizer. Carry out suspension polymerization of the monomeric mixture which contains a polymerization nature monomer and colorant at least, make a colored polymer particle generate, and it ranks second, It can obtain by polymerizing the polymerization nature monomer which can generate the polymer of a glass transition temperature higher than the glass transition temperature of the polymer component which constitutes this colored polymer particle under existence of this colored polymer particle. The monomeric mixture which forms a core is made to contain the specific third class thiol in this invention. Therefore, this invention also includes the polymerization toner and the manufacturing method of such core shell structure.

[0021](1) As a polymerization nature monomer polymerization nature monomer, a monovinyl system monomer is preferred. Specifically Styrene monomer; acrylic acid, such as styrene, vinyltoluene, and alpha-methylstyrene, Methacrylic acid; Methyl acrylate, ethyl acrylate, acrylic acid propyl, Butyl acrylate, 2-ethylhexyl acrylate, acrylic acid dimethylaminoethyl, Methyl methacrylate, ethyl methacrylate, methacrylic acid propyl, Butyl methacrylate, 2-ethylhexyl methacrylate, dimethylaminoethyl methacrylate, The derivative of acrylic acid, such as acrylonitrile, a methacrylonitrile, acrylamide, and methacrylamide, or methacrylic acid; Ethylene, Ethylenic unsaturation monoolefins, such as propylene and butylene; VCM/PVC, Vinyl halide, such as vinylidene chloride, vinyl, fluoridation; Vinyl acetate, Vinyl ester, such as vinyl propionate; Vinyl ether; vinyl methyl ketone, such as vinylmethyl ether and vinylethyl ether, Vinyl ketone, such as methyliso propenyl ketone; nitrogen-containing vinyl compound [ , such as 2-vinylpyridine, 4-vinylpyridine, and N-vinyl pyrrolidone, ]; etc. are mentioned. A monovinyl system monomer is independent, respectively, or can be used combining two or more monomers. It is preferred to use together a styrene monomer and the derivative of acrylic acid (meta) among monovinyl system monomers.

[0022](2) If a cross-linking monomer and/or a cross-linking polymer are used with a cross-linking monomer and a cross-linking polymer polymerization nature monomer, it is effective in a hot offset improvement. A cross-linking monomer is a monomer which has a carbon-carbon unsaturated double bond in which two or more polymerizations are possible. Specifically Aromatic divinyl compound; ethylene glycol dimethacrylate, such as divinylbenzene, divinyl naphthalene, and these derivatives, Diethylene nature unsaturated carboxylic acid ester, such as diethylene-glycol dimethacrylate; 1,4-butanediol, The AKURI (meta) rate of the aliphatic series both-ends alcoholic origins, such as 1,9-nonanediol; compound; etc. which have vinyl groups beyond divinyl compound; 3 piece, such as N,N-divinylaniline and divinyl ether, can be mentioned. As a cross-linking polymer, polyethylene, polypropylene and polyester which have two or more hydroxyl groups, the acrylate of polysiloxane origin (meta), etc. can be mentioned to intramolecular. These cross-linking monomers and a cross-linking polymer are independent, respectively, or can be used combining two or more sorts. A cross-linking monomer and/or a cross-linking polymer are ten or less weight section usually more preferably used at a rate of 0.1 – the amount part of duplex 0.01 to 5 weight section to polymerization nature monomer 100

weight section.

[0023](3) If a macro monomer is used with a macro monomer polymerization nature monomer, balance of preservability, offset tightness, and low temperature fixability can be improved. A macro monomer is a comparatively long linear molecule which has a functional group (for example, an unsaturation group like a carbon-carbon double bond) which can polymerize at the end of a chain. As a macro monomer, oligomer or polymer of 1,000-30,000 usually has a preferred number average molecular weight. If a macro monomer with a small number average molecular weight is used, the surface portion of particle toner will become soft and preservability will fall. On the contrary, if a macro monomer with a large number average molecular weight is used, the melting nature of a macro monomer will be bad and the fixability of a toner will fall.

[0024]As an example of a macro monomer, it is independent in styrene, a styrene derivative, methacrylic acid ester, acrylic ester, acrylonitrile, a methacrylonitrile, etc., or the polymer produced by polymerizing two or more sorts, the macro monomer which has a polysiloxane skeleton, etc. are mentioned. Also in a macro monomer, the polymer which has a glass transition temperature higher than the glass transition temperature of binding resin is preferred, and a copolymer macro monomer and a polymethacrylic-acid-ester macro monomer with styrene, methacrylic acid ester, and/or acrylic ester are especially preferred. When using a macro monomer, the blending ratio receives polymerization nature monomer 100 weight section, is usually depended 0.03 to 5 weight section preferably 0.01 to 10 weight section, and is 0.05 to 1 weight section preferably. When the using rate of a macro monomer is too large, the tendency for fixability to fall is shown.

[0025](4) As colorant colorant, the various paints and color which are used in the field of toners, such as carbon black and a titanium white, can be used. As black colorant, magnetic particle [, such as carbon black, the dyes-and-pigments; cobalt of the Nigrosine base, nickel, a tri-iron tetraoxide, iron oxide manganese, iron oxide zinc and iron oxide nickel, ]; etc. can be mentioned. When using carbon black, since good image quality will be obtained and the safety to the environment of a toner will also increase if primary particle diameter uses what is 20-40 nm, it is desirable.

[0026]As colorant for color toner, a yellow coloring agent, a magenta coloring agent, cyanogen colorant, etc. can be used. as a yellow coloring agent — the C.I. pigment yellow 3, 12, 13, 14, 15, 17, 62, 65, 73, 83, 90, 93, 97, 120, 138, 155, and 180 and the 181; NEFUTORU yellow S. Hansa yellow G, C.I. bat yellow, etc. are mentioned.

[0027]As a magenta coloring agent, they are mentioned by azo pigment, condensed polycyclic pigment, etc. and more specifically, For example, C. The I. pigment red 48, 57, 58, 60, 63, 64, 68, 81, 83, 87, 88, 89, 90, 112, 114, 122, 123, 144, 146, 149, 163, 170, 184, 185, 187, 202, 206, 207, and 209, 251;. C. I. pigment violet 19 grade is mentioned.

[0028]As cyanogen colorant, they are mentioned by a copper-phthalocyanine compound and its derivative, the anthraquinone compound, etc., and more specifically, For example, C.I. pigment blues 2, 3, 6, 15, 15:1, 15:2, 15:3, 15:4, 16, 17, and 60; copper phthalocyanine blue, C.I. bat blue, C.I. acid blue, etc. are mentioned. This colorant is usually preferably used at a rate of one to 20 weight section 0.1 to 50 weight section to polymerization nature monomer 100 weight section which forms binding resin or binding resin.

[0029](5) Use the specific third class thiol as a chain transfer agent in chain transfer agent this invention. The third class thiol used by this invention is the third class thiol with 7-20 carbon atoms with the structure which has at least two tertiary carbon atoms, and the sulfur atom coupled directly with at least one of tertiary carbon atoms of it. A tertiary carbon atom means the carbon atom in which the hydrogen atom has not combined one. An alkyl group or an alkyl group, and sulfhydryl groups, such as a methyl group, have combined with this tertiary carbon atom. The numbers of carbon atoms of the third class thiol are 9-16 preferably from a composite ease or a viewpoint of a operation effect. The number of tertiary carbon atoms is three preferably. The bonding number of a sulfhydryl group is one piece preferably.

[0030]As the third class thiol used by this invention, for example A 2,5,5-trimethyl hexane-2-thiol, A 2,2,4,6,6-pentamethylheptane-4-thiol, a 2,2,4,4,6-pentamethylheptane-6-thiol, A 2,2,4,6,6,8,8-heptamethylnonane-4-thiol, a 2,2,5,8,8-pentamethylnonane-5-thiol, a 2,2,5,5,6,8,8-



heptamethylnonane-6-thiol, etc. are mentioned.

[0031]The using rate of the third class thiol of a chain transfer agent receives polymerization nature monomer 100 weight section, is usually depended 0.1 to 3 weight section preferably 0.05 to 4 weight section, and are 0.5 – the amount part of duplexs preferably. If the using rate of the third class thiol is too small, the reduction effect of fixing temperature will become small, and when too large, preservability shows a fall tendency.

[0032]In this invention, other chain transfer agents (regulator) can be used together if needed in addition to the third class thiol. As other chain transfer agents, for example N-octyl mercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan, n-hexadecylmercaptan, n-tetradecyl mercaptan, a 2,2,4,6,6-pentamethylheptane-4-methylene thiol, A 2,4,6-trimethyl nonane-4-thiol, tridecylmercaptan tetradecyl mercaptan, Mercaptans, such as hexadecylmercaptan; Dimethyl xantho gene disulfide, Xantho gene disulfide, such as diethyl xantho gene disulfide and diisopropyl xantho gene disulfide; Tetramethylthiuramdisulfide, Thiuram disulfide, such as a tetraethylthiuram disulfide and tetrabutylthiuram disulfide; A carbon tetrachloride, halogenated hydrocarbon [ , such as an ethylene bromide, ]; — hydrocarbon [ , such as pentaphenylethane, ]; — an acrolein. alpha, such as methacrolein, beta-unsaturated aldehyde; allyl alcohol; 2-ethylhexyl thioglycolate; TERUPINOREN, alpha-terpinene, beta-terpinene, gamma-terpinene, terpenes [ , such as a dipentene, ]; — alpha-methylstyrene dimer [ , such as 2-4-diphenyl-4-methyl-1-pentene, ]; — 2,5-dihydrofuran etc. are mentioned. Even when it is not necessary to necessarily use it and and uses it, other chain transfer agents are used in a little ranges so that there may not be generating of a bad smell, a fall of offset temperature, a fall of preservability, etc.

[0033](6) It aims at the uniform dispersion to the inside of the particle toner of lubricant and distributed auxiliary agent colorant, etc., Lubricant, such as fatty acid metal salt which consists of fatty acid, such as oleic acid and stearic acid, fatty acid, and metal, such as Na, K, Ca, Mg, and Zn; distributed auxiliary agent [ , such as the Silang system or a titanium system coupling agent ]; etc. may be used. Such lubricant and a dispersing agent are usually used at 1 / about 1000 to 1/1 rate on the basis of the weight of colorant.

[0034](7) In order to raise the electrostatic property of a charge controlling agent toner, it is preferred to make the charge controlling agent of various kinds of positive triboelectric charging or negative triboelectric charging contain in a monomer composition. As a charge controlling agent, for example BONTORON N01 (made by an Orient chemicals company), The Nigrosine base EX (made by an Orient chemicals company), spiro black TRH (made by the Hodogaya chemicals company), T-77 (made by the Hodogaya chemicals company), BONTORON S-34 (made by an Orient chemicals company), BONTORON E-81 (made by an Orient chemicals company), BONTORON E-84 (made by an Orient chemicals company), BONTORON E-89 (made by an Orient chemicals company), BONTORON F-21 (made by an Orient chemicals company), COPY CHRGEX (made by Clariant, LTD.), COPY CHRG NEG (made by Clariant, LTD.), TNS-4-1 (made by the Hodogaya chemicals company), TNS-4-2 (made by the Hodogaya chemicals company), Charge controlling agents, such as LR-147 (made by Japan Carlit Co., Ltd.); JP,11-15192,A, The 4th class ammonium (salt) group content copolymer given in JP,3-175456,A, JP,3-243954,A, etc., Electrification control resin [ , such as a sulfonic acid (salt) group content copolymer of a statement ]; etc. can be used for JP,3-243954,A, JP,1-217464,A, JP,3-15858,A, etc. A charge controlling agent is usually preferably used at a rate of 0.1 to 7 weight section 0.01 to 10 weight section to polymerization nature monomer 100 weight section which forms binding resin or binding resin.

[0035](8) It is preferred to use low softening point material for lowering the fixing temperature of a low-softening-point-material toner, or improving a mold-release characteristic etc. It adds in a monomeric mixture and low softening point material is made to contain in the polymerization toner to generate. When polymerization toner is what has core shell structure, low softening point material is made to contain in the colored polymer particle used as a core.

[0036]As for low softening point material, it is preferred to a styrene monomer general-purpose as the main ingredients of a polymerization nature monomer that it is a thing of fusibility at a room temperature. As such low softening point material, the polyfunctional ester compound which consists of alcohol and carboxylic acid of three or more organic functions, and the



aromatic-carboxylic-acid-ester compound which consists of with a carbon numbers of 15 or more alcohol and carboxylic acid are preferred. When low softening point material is a thing of non-fusibility at a styrene monomer, it is necessary to heat to the temperature more than the melting temperature of low softening point material, and to distribute it at the process of preparing a polymerization nature monomer composition, and. Thus, since it is easy to carry out bleeding to the polymerization toner surface generated by a polymerization process even if it makes it distribute, it is not desirable.

[0037]As alcohol of three or more organic functions, glycerin, pentaerythritol, Fatty alcohol, such as dipentaerythritol and penta glycerol; A fluoroglucitol, Alicyclic alcohols, such as a quercitol and inositol; Aromatic alcohol; D-erythroses, such as tris(hydroxymethyl) benzene, L-arabinose, D-mannose, D-galactose, D-fructose, Sugars, such as L-rhamnose, saccharose, malt sugar, and lactose; sugar-alcohol [ , such as erythritol, D-TOREITTO L-arabite, adonitol, and xylitol, ]; etc. can be mentioned. Pentaerythritol and dipentaerythritol are [ among these ] preferred.

[0038]As an example of alcohol in which the number of carbon atoms is 15 or more, pentadecyl alcohol and cetyl alcohol — it passes and PUTADE sill alcohol, stearyl alcohol, nonadecyl alcohol, eicosyl alcohol, behenyl alcohol, ceryl alcohol, MESHIRIRU alcohol, etc. are mentioned.

[0039]As carboxylic acid, acetic acid, butanoic acid, caproic acid, enanthic acid, caprylic acid, Pelargonic acid, capric acid, undecanoic acid, lauric acid, myristic acid, Stearic acid, margaric acid, arachidic acid, cerinic acid, MERIKISHIN acid, Erica acid, brassidic acid, sorbic acid, linolic acid, linolenic acid, behenyl acid, Aliphatic carboxylic acid, such as Thet Rolle acid and KISHIMENIN acid; Cyclohexane carboxylic acid, Alicyclic carvone acids, such as hexahydro isophthalic acid, hexahydro terephthalic acid, and 3,4,5,6-tetrahydroptal acid; Benzoic acid, Aromatic-carboxylic-acid [ , such as toluic acid, cumin acid, phthalic acid, isophthalic acid, terephthalic acid, trimesic acid, trimellitic acid, and hemimellitic acid, ]; etc. can be mentioned. Also in these, 10-30 aromatic carboxylic acid [ two or more ] is usually preferably preferred for the aliphatic carboxylic acid of 13-25 carboxylic acid, especially this number of carbon atoms, and a carboxyl group for the number of carbon atoms.

[0040]Although polyfunctional ester compounds may differ, respectively and two or more carboxylic acid combined with each hydroxyl group of alcohol of three or more organic functions may be the same, the difference of the maximum of the number of carbon atoms in two or more carboxylic acid and the minimum is five or less thing preferably nine or less suitably. concrete — pentaerythritol tetra Millis Tait, pentaerythritol tetra laurate, dipentaerythritol hexa Millis Tait, and glycerol — doria — RAKIN acid etc. can be mentioned.

[0041]As low softening point material, what is usually 30-200 \*\* in endothermic peak temperature at the time of temperature up within the limits of 50-180 \*\* preferably is desirable in the DSC curve measured with a differential scanning calorimeter (DSC). Polyfunctional ester compounds and aromatic-carboxylic-acid-ester compounds, such as pentaerythritol ester which is in within the limits whose endothermic peak temperature is 60-160 \*\* more concretely, and dipentaerythritol ester which is within the limits of 50-80 \*\*, are mentioned. Especially these polyfunctional ester compound aromatic-carboxylic-acid-ester compounds are preferred in respect of balance with low temperature fixability and a mold-release characteristic.

[0042]The polyfunctional ester compound whose dissolved amount [ as opposed to 100 g of 25 \*\* styrene in a molecular weight ] (g/100gST; 25 \*\*) is not less than 10g and whose acid value is 10 or less mg/KOH more preferably is especially preferred not less than 5g at 600 or more. The dipentaerythritol ester which has especially these physical properties shows higher efficacy to the fall of fixing temperature. Endothermic peak temperature is the value measured by ASTM-D-3418-82. Acid value is the value measured according to JIS-K-1557-1970.

[0043]In the case of an aromatic-carboxylic-acid-ester compound, not less than 5g of dissolved amounts [ not less than 10g of ] (g/100gST; 35 \*\*) to 100 g of styrene measured at 35 \*\* are not less than 15g especially preferably more preferably. Preferably, 2 or less mgKOH/g, the acid value of an aromatic-carboxylic-acid-ester compound is 1.3 or less mgKOH/g especially preferably, and, in many cases, are 1.0 or less mgKOH/g and 0.1 or more mgKOH/g 1.5 or less mgKOH/g. Low softening point material is usually preferably used at a rate of one to 15 weight section 0.1 to 20 weight section to polymerization nature monomer 100 weight section.

[0044](9) Although use of other release agents is unnecessary, it is the purposes, such as prevention from offset, and can make it contain other various release agents by request, in using these in order that low softening point material, such as a release agent polyfunctional ester compound, may act also as a release agent. As a release agent, for example Low molecular weight polyethylene, low molecular weight polypropylene, Low-molecular-weight polyolefine waxes, such as low-molecular-weight polybutylene; Molecular terminal oxidation low molecular weight polypropylene, The low-molecular-weight terminal modified polypropylene which replaced the molecular terminal by the epoxy group, And block polymer of these and low molecular weight polyethylene, molecular terminal oxidation low molecular weight polyethylene, Terminal-modified-polyolefin waxes, such as block polymer etc. of the low molecular weight polyethylene which replaced the molecular terminal by the epoxy group, and these and low molecular weight polypropylene; Candelilla, Vegetable system natural wax, such as carnauba, rice, haze wax, and a jojoba; Paraffin, Synthetic waxes, such as mineral system wax; Fischer Tropsch waxes, such as petroleum system waxes, such as micro crystalline and PETORO lactam, and denaturation wax; Montand of those, a ceresin, and ozocerite; the mixture of these, etc. are illustrated. As for these release agents, it is preferred to use to polymerization nature monomer 100 weight section which forms binding resin or binding resin 0.1 to 20 weight section (further one to 15 weight section).

[0045](10) As a polymerization initiator polymerization initiator, a radical polymerization initiator is used suitably. Specifically Persulfate;4,4'-azobis, such as potassium persulfate and ammonium persulfate (4-cyanovaleric acid), 2,2'-azobis (2-amidinopropane) dihydrochloride, 2,2'-azobis 2-methyl-N-1,1-bis(hydroxymethyl)-2-hydroxyethyl PUROPIO amide, 2 and 2'-azobis (2,4-dimethylvaleronitrile), 2,2'-azobis isobutyronitrile, Azo compounds, such as 1,1'-azobis (1-cyclohexanecarbonitrile); Isobutyryl peroxide, Diacyl peroxide systems, such as 2,4-di-chloro benzoyl peroxide and 3,5,5'-trimethylhexanoyl peroxide; Bis(4-t-butylcyclohexyl)peroxy di-carbonate, Di-n-propyl peroxy di-carbonate, di-isopropyl \*\*\*\*\*- carbonate, di-2-ethoxyethyl peroxy di-carbonate, JI (2-ethylethyl peroxy) di-carbonate, \*\*-\*\*\*\*\* butylperoxy di-carbonate, Peroxy di-carbonate, such as JI (3-methyl-3-methoxy butylperoxy) di-carbonate; (alpha and alpha-bis-neo decanoly peroxy) Diisopropylbenzene, Cumil-peroxy-neodecanoate, 1, 1', 3, and 3'-tetramethyl butylperoxyneodecanoate, 1-cyclohexyl-1-methylethyl peroxy neo decanoate, T-hexylperoxy neodecanoate, t-butylperoxy neodecanoate, t-hexyl peroxy pivalate, t-butylperoxy perpivalate, Methylethyl peroxide, di-t-butyl peroxide, acetyl peroxide, JIKUMIRU peroxide, lauroyl peroxide, benzoyl peroxide, Other peroxides, such as t-butylperoxy2-ethylhexanoate, di-isopropyl peroxy dicarbonate, di-t-butyl peroxyisophthalate, and t-buthylperoxy isobuthylate, are illustrated. The redox initiator which combined these polymerization initiators and a reducing agent can also be used.

[0046]Among these, an oil-soluble radical initiator meltable to a polymerization nature monomer is preferred, and can also use a water-soluble initiator together with this if needed. The using rate of a polymerization initiator receives polymerization nature monomer 100 weight section, is usually depended 0.3 to 15 weight section preferably 0.1 to 20 weight section, and is 0.5 to 10 weight section preferably. A molecular weight will become low if too large [ when this using rate is too small, a rate of polymerization is slow and ]. Although it can add beforehand in a monomer composition, polymerization initiators are the purposes, such as avoiding preliminary polymerization, and can also be added in suspension after the end of a granulation stage of the monomer composition in the drainage system carrier fluid inside of the body. The using rate of a polymerization initiator is a drainage system carrier fluid object standard, and is usually about 0.001 to 3 % of the weight.

[0047](11) As dispersion stabilizer used for dispersion stabilizer this invention, Sulfate, such as barium sulfate and calcium sulfate; Barium carbonate, calcium carbonate, carbonate [ such as magnesium carbonate, ]; — phosphate [ such as calcium phosphate ]; — an aluminum oxide. Metallic oxides, such as titanium oxide; Aluminium hydroxide, magnesium hydroxide, Metal hydroxide, such as a ferric hydroxide; surface-active agent [ such as water soluble polymer; anionic surface-active agents, such as polyvinyl alcohol, methyl cellulose, and gelatin, a nonionic surface-active agent, and an ampholytic surface active agent, ]; etc. can be mentioned. Metallic

compounds, such as sulfate, carbonate, a metallic oxide, and metal hydroxide, are preferred, and colloid of the metallic compounds of difficulty water solubility is [ among these ] more preferred. Since especially colloid of metal hydroxide of difficulty water solubility can narrow particle size distribution of particle toner and its clear nature of a picture improves, it is preferred.

[0048]Colloid of the difficulty water solubility metal hydroxide obtained by adjusting the pH of the solution of a water-soluble polyvalent-metallic-salt compound to seven or more although colloid of difficulty water soluble metallic compounds does not have the restriction by the process, Colloid of the metal hydroxide of difficulty water solubility especially generated by the reaction in the aqueous phase of a water-soluble polyvalent-metallic-salt compound and a hydroxylation alkaline metal is preferred. Number particle-size-distribution  $D_{50}$  (50% accumulated of number particle size distribution) is 0.5 micrometer or less, and, as for colloid of difficulty water soluble metallic compounds, it is preferred that  $D_{90}$  (90% accumulated of number particle size

distribution) is 1 micrometer or less. If the particle diameter of colloid becomes large too much, the stability of a polymerization will collapse and the preservability of a toner will fall.

[0049]This dispersion stabilizer is usually preferably used at a rate of 0.3 to 10 weight section 0.1 to 20 weight section to polymerization nature monomer 100 weight section. If there are too few these using rates, it will be difficult to acquire sufficient polymerization stability, and will become easy to generate a polymerization aggregate. On the contrary, if there are too many these using rates, the particle size distribution of particle toner spreads by the increase in particles, or aqueous solution viscosity will become large and polymerization stability will become low.

[0050](12) The manufacturing method polymerization toner of a colored polymer particle can be obtained as a colored polymer particle by carrying out suspension polymerization of the monomeric mixture which contains a polymerization nature monomer and colorant at least in the drainage system carrier fluid body containing dispersion stabilizer. Mix a polymerization nature monomer, colorant, the third class thiol, a charge controlling agent, low softening point material, etc., it is made to more specifically distribute uniformly using a bead mill etc., and the monomeric mixture which is oily mixed liquor is prepared. Subsequently, after throwing this monomeric mixture into the drainage system carrier fluid inside of the body containing dispersion stabilizer, stirring with an agitator and the particle diameter of the drop of a monomeric mixture becoming fixed, a polymerization initiator is supplied and it is made to shift into the drop of a monomeric mixture. Next, the drop of a monomeric mixture is corned even to a still more detailed drop using the mixed device which has high shearing. Thus, after corning even to the detailed drop which has the particle diameter of the grade which matches mostly in the particle diameter of the polymerization toner to generate, it usually polymerizes at the temperature of 30–200 \*\*. Thus, a colored polymer particle is made to generate. The generated colored polymer particle is used as polymerization toner.

[0051](2) The polymerization toner of the manufacturing method core shell structure of the polymer particle of core shell structure can be manufactured by methods, such as the spray dry method, an interface reaction method, an in situ polymerization method, and a phase separation method. Especially an in situ polymerization method and a phase separation method have well preferred manufacturing efficiency. in In the situ polymerizing method, in the drainage system carrier fluid body containing dispersion stabilizer. The polymer particle (polymerization toner) of core shell structure can be obtained by using as a core the colored polymer particle obtained by carrying out suspension polymerization of the monomeric mixture which contains a polymerization nature monomer and colorant at least, and carrying out suspension polymerization of the polymerization nature monomer for shell under existence of this core. The third class thiol is made to contain in a monomeric mixture when manufacturing the colored polymer particle used as a core in this invention.

[0052]If a water-soluble polymerization initiator is added when adding the polymerization nature monomer for shell in a polymerization reaction system, it will become easy to generate a polymer particle with a core shell type structure. As a water soluble polymerization initiator, persulfate;4,4'-azobis, such as potassium persulfate and ammonium persulfate (4-cyanovaleric

acid), 2,2'-azobis (2-amidinopropane) dihydrochloride, Azo initiators, such as 2,2'-azobis 2-methyl-N-1,1'-bis(hydroxymethyl)-2-hydroxyethyl PUROPIO amide; combination [ of oil-soluble initiators such as cumene peroxide, and a redox catalyst ]; etc. can be mentioned. The quantity of a water soluble polymerization initiator is a drainage system carrier fluid object standard, and is usually 0.001 to 3 % of the weight.

[0053]The blocking resistance of polymerization toner, i.e., preservability, can be improved by using the polymerization nature monomer which can generate the polymer of a glass transition temperature higher than the glass transition temperature of the polymer component which constitutes the colored polymer particle of a core as a polymerization nature monomer for shell. As a polymerization nature monomer for cores, that in which glass transition temperature can usually generate 60 \*\* or less of about 40-60 \*\* polymers preferably is preferred. As a polymerization nature monomer for shell, not less than 10 \*\* of not less than 20 \*\* and the things which can generate the polymer of a more desirable glass transition temperature high not less than 30 \*\* are preferably more preferred than the glass transition temperature of the polymer component which forms a core. The glass transition temperature of the polymer formed from the polymerization nature monomer for shell of 110 \*\* or less of excess of 60 \*\* is [ usually and 120 \*\* or less of excess of 50 \*\* ] 80-105 \*\* more preferably. Glass transition temperature is a value computed by calculation in accordance with a conventional method from the kind and using rate of each monomer.

[0054]The polymerization nature monomer for cores and the polymerization nature monomer for shell are usually used by the weight ratio of 80:20 to 99.9:0.1. A preservability improvement effect is small in too little [ the rate of the polymerization nature monomer for shell ], and the improvement effect of the reduction of fixing temperature by being excessive becomes small conversely. the thickness of shell — usually — 0.003-0.5-micrometer 0.001-1.0 micrometer is 0.005-0.2 micrometer more preferably.

[0055]2. The toner for electrostatic charge image development of toner this invention for electrostatic charge image development can be preferably obtained by the above-mentioned polymerizing method. 2-11 micrometers of volume average particle diameter (dv) of the polymerization toner (the polymerization toner of core shell structure is included) obtained by the manufacturing method of this invention are 1-12 micrometers usually 3-10 micrometers more preferably. When using it for the use which acquires a high definition picture especially, 2-9 micrometers of volume average particle diameter of polymerization toner can be preferably made it is more desirable and small even to 3-8 micrometers. particle-size-distribution = volume-average-particle-diameter (dv) / number average particle diameters of the polymerization toner obtained by the manufacturing method of this invention (dp) — usually — it is 1.3 or less more preferably 1.5 or less 1.7 or less. Resolution can be raised by adjusting the volume average particle diameter and particle size distribution of polymerization toner to said within the limits.

[0056]Since the third class thiol is used as a chain transfer agent at the time of the composition, binding resin of the toner for electrostatic charge image development of this invention is the polymer which the alkylthio group resulting from the chain transfer reaction of this the third class thiol combined. An alkylthio group is an alkylthio group with 7-20 carbon atoms with the structure which has at least two tertiary carbon atoms, and the sulfur atom coupled directly with at least one of tertiary carbon atoms of it. Although the connecting position in particular of an alkylthio group is not restricted, it is usually molecular chain terminals of a polymer, in view of the mechanism of the chain transfer of the third class thiol.

[0057]If needed, for the purpose of the improvement in mobility, polish nature, etc., it can mix with a general-purpose external additive, and the polymerization toner obtained by the manufacturing method of this invention can be used. As an external additive, an inorganic particle and/or organic resin particles are mentioned. As an inorganic particle, a silica dioxide, an aluminum oxide, titanium oxide, a zinc oxide, tin oxide, barium titanate, strontium titanate, etc. are mentioned. As organic resin particles, methacrylate polymer particles, acrylic ester polymer particles, The core shell type particles etc. in which styrene methacrylic-acid-ester copolymer particles, styrene acrylic ester copolymer particles, zinc stearate, calcium stearate, and a core were formed in with the methacrylic-acid-ester copolymer, and shell was formed with the

styrene polymer are mentioned. An inorganic oxide particle, especially silica dioxide particles are [ among these ] preferred. Especially the silica dioxide particles by which could carry out hydrophobing processing of the surface of these particles, and hydrophobing processing was carried out are preferred. Although the quantity in particular of an external additive is not limited, it is usually 0.1 to 6 weight section to polymerization toner 100 weight section.

[0058]An external additive may be used combining two or more sorts. When using combining an external additive, the method of combining the inorganic particles or inorganic particle which differs in mean particle diameter, and organic resin particles is preferred. Adhesion of an external additive is usually performed by putting an external additive and polymerization toner into mixers, such as a Henschel mixer, and stirring them.

[0059]The softening temperature (Ts) of the toner measured with the flow tester is 62-67 \*\*, and, as for the toner for electrostatic charge image development of this invention (the thing containing an external additive is included), it is preferred that the outflow starting point (Tfb) is not less than 110 \*\*. Heating a toner sample with a fixed heating rate using a flow tester, give constant load to a plunger, it is made to extrude from a nozzle, and the amount of descent-temperature curve of a flow tester's plunger is drawn by this (a temperature graduation is a horizontal axis). The height in the standup time of the beginning of this curve is called softening temperature (temperature;Ts in which it softened and the internal gap disappeared). If it furthermore heats, a curve will rise on a steep slope, but it flows out and the time is called the starting point (temperature into which the fused toner flows out of a nozzle; Tfb). The details of the measuring method of the melting characteristic using a flow tester are mentioned later.

[0060]It excels in low temperature fixability, so that the softening temperature (Ts) temperature of a toner is low, and offset generating temperature becomes high and it becomes difficult to generate offset, so that outflow starting point (Tfb) temperature is high. Even if softening temperature (Ts) temperature is low, when outflow starting point (Tfb) temperature is also low, it becomes easy to generate offset. The softening temperature (Ts) of the toner measured with the flow tester has the more preferred range of 63-66 \*\*, as for the outflow starting point (Tfb), it is more preferred that it is not less than 120 \*\*, and it is preferred that it is especially not less than 130 \*\*. As a chain transfer agent, these desirable melting characteristics can be given to a toner by using said the specific third class thiol.

[0061]If the toner for electrostatic charge image development of this invention (especially polymerization toner of core shell structure) is used, fixing temperature can be more preferably reduced in temperature of about 100-140 \*\* by 80-160 \*\*, and, moreover, offset generating temperature can be maintained to a not less than 200 \*\* elevated temperature. The toner for electrostatic charge image development of this invention is excellent in preservability and mobility, does not have generating of a pungent smell at the time of printing, and can form the picture of good image quality with high resolution.

[0062]

[Example]Although an example and a comparative example are given to below and this invention is explained more concretely, this invention is not limited only to these examples. A part and % are weight references as long as there is no notice especially. The measuring method of the physical properties in an example and a comparative example is as follows.

[0063](1) Particle diameter, volume average particle diameter (dv) of a particle-size-distribution polymer particle, and particle size distribution [Volume-average-particle-diameter (dv) / number average particle diameters (dn)] were measured by the multi-sizer (made by Beckman Coulter). Measurement by this multi-sizer was performed on measurement-particles number =100,000 piece conditions diameter =of aperture100micrometer, the medium = iso ton II, and concentration =10%.

[0064](2) If thick, it can measure with a multi-sizer or an electron microscope, but like an example and a comparative example, when thin, compute the thickness of the shell of the polymerization toner of shell thickness core shell structure using the following formulas.

$$x=r(1+s/100\rho)^{1/3}-r(1)$$

However, the radius x of the mean particle diameter (volume particle diameter of a multi-sizer:

micrometer) of the core-polymer particles before addition of the monomer for r:shell: Shell thickness (micrometer)

s: The number of addition parts of the monomer for shell (number of copies to 100 copies of monomers for cores)

rho: — density [ of a shell polymer ] ( $\text{g}/\text{cm}^3$ ); — usually — as  $\rho = 1.0$  — calculation.

[0065](3) Using the melting characteristic quantity-ized type flow tester (the Shimadzu make, CFT-500C), in accordance with the conventional method, the amount of plunger descent-temperature curve was created by the following measuring condition, and each temperature of the softening temperature ( $T_s$ ) of a toner and the outflow starting point ( $T_{fb}$ ) was searched for. Starting temperature: Every 35.0 \*\*, arrival temperature:250.0 \*\*, and time-between-measurements:2.5 \*\*/, heating-rate:3.0 \*\* /, and min, preheating time:300sec, and test

force:10.0kgf/cm<sup>2</sup>, nozzle hole diameter:0.50mm, nozzle 1.00 mm, and piston:1.0cm<sup>2</sup>. [ in length ]

[0066](4) The printer (printing speed = a part for 16-sheet/) of commercial one ingredient of nonmagnetic development system is used on the conditions of the printing test temperature of 23 \*\*, and 50% of relative humidity, The polymerization toner evaluated to the developer of this printer was put in, continuous printing was performed from the first stage, and printing density (initial printing density) was measured with the reflection density plan (made in Macbeth). Fogging on the photo conductor of a nonimage area was investigated with the whiteness degree plan (made by Nippon Denshoku) after the continuous printing of 20,000 sheets. Fogging made adhesive tape (Sumitomo 3M Scotch whisky mending tape 810-3-18) adhere to the nonimage area on a photo conductor, and was investigated. After making adhesive tape adhere to the nonimage area of the photo conductor before printing, it specifically removes, and this is stuck on a print form, and the whiteness degree A is measured. On the other hand, after making adhesive tape adhere to the nonimage area of the photo conductor after printing, it removes, and this is stuck on a print form, and the whiteness degree B is measured. Fogging (%) is computable by  $A - B$ . Continuous printing was performed with printing density 5%.

[0067](5) The fixing examination was done using the printer converted so that the temperature of the fixing roll part of the printer (printing speed = a part for 16-sheet/) of one ingredient of nonmagnetic development system of fixing temperature marketing could be changed. The temperature of the fixing roll of a modified printer was changed, the fixing rate of the developer in each temperature was measured, and the fixing examination was done by asking for the relation of a temperature-fixing rate. The fixing rate was calculated from the ratio of the image concentration before and behind tape peeling operation of the black solid field in the examination paper which was neglected for more than 5 minutes in order to stabilize the temperature of a fixing roll, when changing temperature, and was printed with the modified printer after that. That is, if image concentration in front of ID and after tape exfoliation is carried out ID back, the fixing rate can compute the image concentration before tape exfoliation from a following formula.

fixing rate (%) = (after [ ID ] / before ID) x 100 — here, with tape peeling operation. Stick adhesive tape (Sumitomo 3M Scotch whisky mending tape 810-3-18) on the measured part of an examination paper, it is made to press and adhere in a constant pressure, and they are a series of operations of exfoliating adhesive tape in the direction which met paper with constant speed, after that. Image concentration was measured using the Macbeth reflection type image concentration measuring apparatus. In this fixing examination, fixing roll temperature applicable to 80% of a fixing rate was made into the fixing temperature of a developer.

[0068](6) Changed fixing temperature as well as hot offset generating temperature fixing temperature, black solid was made to print, and fixing roll temperature when offset occurred was made into hot offset generating temperature.

[0069](7) A fluid ratio (evaluation of mobility and preservability)

An opening puts from a top three sorts of sieves which are 150 micrometers, 75 micrometers, and 45 micrometers respectively on this order, and weighs precisely and carries the polymerization toner 4g measured on the top sieve. Subsequently, after vibrating three sorts of these piled-up sieves for 15 seconds on condition of the oscillating intensity graduation 4 using granular material measuring apparatus (the Hosokawa micron company make, trade name



"powder tester"), the weight of the developer which remained on each sieve is measured. A fluid value is computed by putting each measured value into following formula \*\*, \*\*, and \*\*, and calculating the value of a, b, and c, next putting these values into formula \*\*. It measured 3 times per one sample, and the average value was calculated.

\*\*  $a = [(\text{polymer weight (g) which remained in a 150-micrometer screen}) / 4g] \times 100$  \*\*  
 $b = [(\text{polymer weight (g) which remained in a 75-micrometer screen}) / 4g] \times 100 \times 0.6$  \*\*  
 $c = [(\text{polymer weight (g) which remained in a 45-micrometer screen}) / 4g] \times 100 \times 0.2$  \*\*  
 mobility (%) =  $100 - (a + b + c)$

The mobility in early stages of a developer ( $F_0$ ) is measured as mentioned above. On the other hand, after putting a developer into a container and saving for five days at 50 \*\*, mobility ( $F_1$ ) is measured in a similar manner. The fluid ratio ( $F_1/F_0$ ) was computed and it was considered as the index of preservability (blocking resistance) and mobility.

[0070](8) In the printing examination of the evaluation above-mentioned of a bad smell, organic-functions evaluation of the bad smell near a print paper exit was carried out by five healthy people, and the following standard estimated the bad smell.

C:3 or more persons as whom A:5 persons feel that a bad smell is, and B:1-2 persons who are not sense a bad smell sense a bad smell.

[0071][Example 1]

(1) The polymerization nature monomer for cores which consists of 80.5 copies of preparation styrene and 19.5 copies of n-butyl acrylate of a monomer composition (calculation Tg of the copolymer obtained = 55 \*\*), a polymethacrylic-acid-ester macro monomer (the Toagosei chemical industry company make.) A trade name "AA6", Tg = 94 \*\* 0.3 copy, 0.6 copy of divinylbenzene (55% of industrial use purity), 1.0 copy of 2,2,4,6,6-pentamethylheptane-4-thiol, 7.0 copies of carbon black (the Mitsubishi Chemical make, trade name "#25B"), 1.0 copy of charge controlling agent (the Hodogaya chemicals company make, trade name SUPIRON black TRH), a release agent [Shell and the product made by MDS, a trade name "FT-100"] After stirring two copies with usual agitating equipment and mixing, uniform dispersion was carried out with the media type dispersion machine.

[0072](2) In the solution which dissolved 10.2 copies of magnesium chlorides (water-soluble polyvalent metallic salt) in 250 copies of ion exchange water at the preparation room temperatures of the drainage system carrier fluid object. It added gradually under stirring of the solution which dissolved 6.2 copies of sodium hydroxide (hydroxylation alkaline metal) in 50 copies of ion exchange water, and magnesium hydroxide colloid (metal hydroxide colloid of difficulty water solubility) dispersion liquid were prepared. When the particle size distribution of the generated above-mentioned colloid was measured with the micro track particle-size-distribution measuring instrument (made by Nikkiso Co., Ltd.),  $D_{50}$  (50% accumulated of number particle size distribution) was 0.35 micrometer, and  $D_{90}$  (90% accumulated of number particle size distribution) of particle diameter was 0.84 micrometer. In measurement by this micro track particle-size-distribution measuring instrument, it carried out on condition of medium = ion exchange water for measurement-range = 0.12-704micrometer, and measuring time = 30 seconds.

[0073](3) Three copies of preparation methyl methacrylate (calculation Tg = 105 \*\*) and 100 copies of water of the polymerization nature monomer for shell were micro-disperse-ization-processed with the ultrasonic emulsification machine, and the water dispersion of the polymerization nature monomer for shell was obtained.  $D_{90}$  was 1.6 micrometers, when the particle diameter of the drop of the polymerization nature monomer for shell in a water dispersion was applied by 3% of concentration into 1% hexametaphosphoric acid sodium solution and measured the obtained drop with the micro track particle-size-distribution measuring instrument.

[0074](4) In the magnesium hydroxide colloidal dispersion liquid obtained by the granulation stage above (2) at a room temperature. It agitates until it throws in the monomeric mixture obtained above (1) and a drop is stabilized, there — as a polymerization initiator — t-butylperoxy2-ethylhexanoate (the Nippon Oil & Fats Co., Ltd. make.) Trade name "par butyl O" Quantity



shearing churning during 10 minutes was carried out at the number of rotations of 15,000 rpm after adding five copies using EBARAMAIRUDA (the Ebara Corp. make, trade name "MDN303 V type"), and the drop of the monomeric mixture was corned.

[0075](5) When the water dispersion of the monomeric mixture corned by the suspension polymerization process above (4) was put into the reactor equipped with stirring wings, a polymerization reaction was started at 95 °C and polymerization conversion reached to about 100%, it sampled and the particle diameter of the colored polymer particle (core) was measured. As a result, the volume average particle diameter of the core particle was 7.0 micrometers. Next, the polymerization nature monomer for shell and the water-soluble initiator which were prepared above (3) [The Wako Pure Chem make, trade name "VA-086"; 2,2' azobis [the 2-methyl- N -(2-hydroxy ethyl)- propionamide]] 0.3 copy was dissolved in 65 copies of distilled water, and it was put into the reactor. After continuing a polymerization for 8 hours, the reaction was suspended and the water dispersion of pH 9.5 polymer particle was obtained. Stirring the water dispersion of the polymer particle obtained by the above, pH of the system was set to about 5.0 with sulfuric acid, and acid cleaning (for 25 °C and 10 minutes) was performed. Subsequently, it filtered and dried, and after drying, wash water was sprinkled and backwashing by water was performed. Then, the oven (45 °C) performed 2 day-and-night desiccation, and the polymer particle was obtained.

[0076](6) To 100 copies of polymer particles of the core shell structure acquired by the developer above (5), 0.8 copy of silica (Degussa AG make; trade name "R972") with a mean particle diameter of 14 nm which carried out hydrophobing processing was added, it mixed to them using the Henschel mixer, and one ingredient of nonmagnetic developer was obtained. A result is shown in Table 1.

[0077][Example 2] In the preparation process of (1) monomer composition of Example 1, It carried out like Example 1 except having changed the addition of the divinylbenzene of a cross linking agent into 0.7 copy from 0.6 copy, and having changed the addition of the 2,2,4,6,6-pentamethylheptane-4-thiol of a chain transfer agent into 2.0 copies from 1.0 copy, respectively. A result is shown in Table 1.

[0078][Example 3] In the preparation process of (1) monomer composition of Example 1, It carried out like Example 1 except having changed SUPIRON black TRH of the charge controlling agent into FCA626N (electrification control resin [ by FUJIKURA KASEI CO., LTD. ], and Mw= about 27,000, Mn= about 8,000, sulfonic group addition structural unit ratio 7-mol% of styrene acrylic ester resin). A result is shown in Table 1.

[0079][Example 4] In the preparation process of (1) monomer composition of Example 1, It carried out like Example 1 except having changed SUPIRON black TRH of the charge controlling agent into FCA626N, and having changed the "FT-100" 2 copy of the release agent into the dipentaerythritol hexa Millis Tait 10 copy, respectively. A result is shown in Table 1.

[0080][Comparative example 1] In the preparation process of (1) monomer composition of Example 1, it carried out like Example 1 except having changed the 2,2,4,6,6-pentamethylheptane-4-thiol of the chain transfer agent into t-dodecyl mercaptan. A result is shown in Table 1.

[0081][Comparative example 2] In the comparative example 1, it carried out like the comparative example 1 except having changed the addition of t-dodecyl mercaptan into 2.0 copies from 1.0 copy. A result is shown in Table 1.

[0082]

[Table 1]

	実 施 例				比 較 例	
	1	2	3	4	1	2
<b>コア (部)</b>						
スチレン	80.5	80.5	80.5	80.5	80.5	80.5
n-BA (*1)	19.5	19.5	19.5	19.5	19.5	19.5
マクロモノマー	0.3	0.3	0.3	0.3	0.3	0.3
架橋剤 (DVB) (*2)	0.6	0.7	0.6	0.6	0.6	0.7
着色剤 (CB) (*3)	7.0	7.0	7.0	7.0	7.0	7.0
帯電制御剤 (*4)	TRH	TRH	FCA	FCA	TRH	TRH
	1.0	1.0	1.0	1.0	1.0	1.0
離型剤 (*5)	FT-100	FT-100	FT-100	DPEHM	FT-100	FT-100
	2.0	2.0	2.0	10.0	2.0	2.0
連鎖移動剤						
PMHT (*6)	1.0	2.0	1.0	1.0	-	-
TDM (*7)	-	-	-	-	1.0	2.0
<b>シェル (部)</b>						
MMA (*8)	3.0	3.0	3.0	3.0	3.0	3.0
<b>重合トナー</b>						
体積平均粒径 (dv)	7.1	7.1	7.2	7.1	7.2	7.1
粒径分布 (dv/dn)	1.20	1.20	1.19	1.21	1.20	1.21
シェル厚 (μm)	0.04	0.04	0.04	0.04	0.04	0.04
溶融特性						
Ts (°C) (*9)	63.4	64.0	65.1	64.5	62.7	60.5
Tfb (°C) (*10)	132	148	138	135	125	110
<b>現像剤特性</b>						
印字濃度	1.42	1.45	1.43	1.45	1.43	1.45
2万枚印字後						
カブリ	1.2	0.8	1.3	1.5	1.5	1.4
定着温度 (°C)	135	135	140	125	165	130
ホットオフセット						
発生温度 (°C)	220	220	220	220	220	150
保存 (50°C/5日) 前						
後の流動性比	0.98	0.95	1.16	0.99	0.97	0.35
印字臭気	A	A	A	A	B	C

## [0083](Footnote)

(\*1) n-BA:n-butyl acrylate (\*2) DVB : divinylbenzene (55% of purity)

CB:carbon black (\*4) charge controlling agent TRH : (\*3) The Hodogaya chemicals company make, SUPIRON Black TRHFCA: The FUJIKURA KASEI CO., LTD. make, electrification control resin FCA626N (\*5) release agent FT-100 : Shell and the product made by MDS, Fischer Tropsch wax DPEHM:dipentaerythritol hexa Millis Tait (\*6) — PMHT:2,2,4,6,6-

pentamethylheptane-4-thiol (\*7) TDM:t-dodecyl mercaptan (\*8) MMA:methyl methacrylate. (\*9) Ts: — softening temperature (\*10) Tfb: of a toner — the outflow starting point of a toner [0084]

By using the specific third class thiol as a chain transfer agent so that clearly from the result of Table 1 (Examples 1-4), Fixing temperature is reduced, moreover, offset temperature is maintained to an elevated temperature, in addition, there is no bad smell, and the toner for electrostatic charge image development which can form a high-definition picture can be obtained. On the other hand, if t-dodecyl mercaptan which is a general-purpose chain transfer agent is used, When there are few the additions (comparative example 1), fixing temperature cannot be lowered, but when there are many additions (comparative example 2), the offset temperature of that to which fixing temperature can be reduced falls remarkably, moreover the bad smell at the time of printing becomes severe, and preservability also falls.

## [0085]

[Effect of the Invention]According to this invention, fixing temperature is low and Energy saving, printing, and improvement in the speed of a copy, It can respond to colorization etc. and, moreover, excels in preservability and mobility, and offset temperature is high, there is also no generating of a bad smell, and the toner for electrostatic charge image development which can

form the picture of good image quality with high resolution is provided. The toner for electrostatic charge image development of this invention can be used with various image forming devices as a developer for developing an electrostatic latent image in a xerography, an electrostatic printing method, an electrostatic recording method, etc.

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**TECHNICAL FIELD**

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[Field of the Invention]This invention relates to a toner for electrostatic charge image development used for the development of the electrostatic latent image formed in a xerography, an electrostatic recording method, an electrostatic printing method, etc., and a manufacturing method for the same.

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PRIOR ART

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[Description of the Prior Art]In a xerography, an electrostatic recording method, an electrostatic printing method, etc., the toner (toner for electrostatic charge image development) is used as a developer for visualizing the electrostatic latent image formed on the photo conductor. A toner is a coloring particle containing binding resin, colorant, a charge controlling agent, a release agent, etc. The manufacturing method of a toner is divided roughly into pulverizing method and the polymerizing method. Pulverizing method is a method of carrying out melt kneading, ranking second, grinding and classifying each ingredient, such as binding resin and colorant, and manufacturing a toner (pulverizing method toner). In pulverizing method, since it is necessary to use the thing of construction material with the brittleness which is easy to be ground as binding resin, it is generated by a lot of impalpable powder according to a grinding process. Although a classification must remove such impalpable powder, a process is complicated and, moreover, the yield becomes low. Since a pulverizing method toner is construction material with weak binding resin, pulverization is carried out within devices, such as a copying machine, at the time of use, and, as a result, image quality deteriorates.

[0003]On the other hand, the polymerizing method is a method of making the polymer particle containing colorant etc. generating, by carrying out suspension polymerization of the monomeric mixture which contains a polymerization nature monomer, colorant, a charge controlling agent, a release agent, etc. in the drainage system carrier fluid body containing dispersion stabilizer. In the polymerizing method, the obtained colored polymer particle can be used as a toner (polymerization toner). thus, the polymerizing method — if — since a grinding process is not needed, the material which can form the polymer which is hard to be ground as a polymerization nature monomer can be chosen. since polymerization toner is a globular form substantially, it is excellent in mobility, and, moreover, particle size distribution boils it markedly as compared with a pulverizing method toner, and it is sharp.

[0004]It is minute to the toner for electrostatic charge image development, the picture of the outstanding high-concentration image quality can be formed in it, and image quality does not deteriorate in it by change of environment, such as temperature and humidity, either, but, moreover, it is required for it are continuous printing, that a consecutive copy should be possible, etc. In addition to these characteristics, the toner for electrostatic charge image development is urged for it to be able to respond to improvement in the speed of that it can contribute to energy saving, printing, and a copy, to be able to respond to full color-ization, etc. these days. Therefore, moreover, in addition, the toner for electrostatic charge image development is urged to improve fixability, such as a fall of fixing temperature, without maintaining high definition and spoiling preservability.

[0005]Specifically in image forming devices with which the toner for electrostatic charge image development is used, such as a copying machine of an electrophotographing system, and a printer, reduction of power consumption is attained these days. The process of consuming energy also especially in an electrophotographing system is a fixing process for being established, after transferring the toner image on a photo conductor on transfer materials, such as paper. Generally, in the fixing process, in order to fix a toner image on a transfer material, the fixing roll and fixing belts which were heated at not less than 150 \*\* are used, and the electrical

and electric equipment is used as the energy source. Lowering this fixing temperature is called for from a viewpoint of energy saving.

[0006]Improvement in the speed of printing speed or copy speed is called for these days. While composite-izing of an image forming device and the network of a personal computer progress especially, the demand to high speed printing or high speed copying is increasingly stronger. Therefore, in the high speed printer or the high speed copying machine, shortening of fixing time is needed.

[0007]In the design of the toner for electrostatic charge image development, there is a method of reducing the glass transition temperature ( $T_g$ ) of binding resin as the technique of meeting the demand from such an image forming device. However, if  $T_g$  of binding resin is reduced, all over preservation of a toner, or the toner box of a developer, particle toner will cause blocking mutually, and will be floc, and it will be a toner what is called with bad preservability.

[0008]These days, the color printing and color copying art by an electrophotographing system are developed. In order to perform color printing and color copying, usually the electrostatic latent image on a photo conductor was developed using the color toner of 3 thru/or 4 colors, and was transferred at once or one by one on the transfer material, and it is established after an appropriate time. For this reason, the thickness of the toner established compared with a monochrome image becomes thick. In order to make it color to a predetermined color tone with mixed colors, it is required at the time of fixing to carry out melting of two or more overlapping color toner uniformly.

[0009]Therefore, it is necessary to make it easy to design the melt viscosity near fixing temperature low compared with the conventional thing, and to fuse in color toner. There are methods, such as making the molecular weight of binding resin low, or lowering  $T_g$  as the technique of making melt viscosity of a toner low, compared with the conventional toner. However, by any method, it will be easy to cause blocking and will be a toner with bad preservability. Thus, adoption of the refining technique of the toner corresponding to energy saving, improvement in the speed of printing or a copy, and colorization will reduce the preservability of a toner.

[0010]Conventionally, the fixing temperature of the toner for electrostatic charge image development is lowered, and the toner which has core shell structure is simultaneously proposed as the technique of raising blocking resistance. It is the method of forming the particle toner (it is also called capsule toner) of the structure which specifically used as the core the coloring particle which contains binding resin and colorant at least and in which  $T_g$  covered this core with high resin. In the polymerizing method, carry out suspension polymerization of the polymerization nature monomeric mixture which contains a polymerization nature monomer and colorant at least, make a colored polymer particle generate, and it ranks second, The method of making the polymer particle of core shell structure generate is known by polymerizing the polymerization nature monomer which can generate the polymer of  $T_g$  higher than  $T_g$  of the polymer component which constitutes this colored polymer particle under existence of this colored polymer particle. If this technique is adopted, the polymer particle of the structure which covered the circumference of the colored polymer particle (core) of low  $T_g$  with the thin polymer layer (shell) of high  $T_g$  can be obtained.

[0011]The toner of such core shell structure can control blocking of toners by the shell which consists of a polymer layer of high  $T_g$  while being able to lower fixing temperature by making low enough  $T_g$  of the binding resin which constitutes a core. However, since the temperature which offset generates would also become low if  $T_g$  of the binding resin which constitutes a core is lowered in order to lower fixing temperature even if it is a toner of such core shell structure, it was difficult to obtain high definition.

[0012]In order to adjust the molecular weight of binding resin, conventionally, the method of polymerizing a polymerization nature monomer under existence of chain transfer agents, such as *n*-dodecyl mercaptan, is known (for example, paragraph number [0032] of JP,11-38674,A). When binding resin is manufactured using a chain transfer agent, \*\* which makes the molecular weight of binding resin low is made, and since the reduction in  $T_g$  is also easy, improvement in the melting characteristic of a toner and reduction of fixing temperature are expected.

[0013]However, in order that mercaptans proposed as a typical chain transfer agent by the technical field of the toner from the former, such as t-dodecyl mercaptan and n-dodecyl mercaptan, might remain in binding resin, there was a problem that a toner generated a pungent smell. If the amount of these mercaptans used is lessened, fixing temperature of a toner of what can control the bad smell of a toner cannot fully be lowered. On the other hand, if the amount of these mercaptans used is increased, in addition to the pungent smell of what can fully lower the fixing temperature of a toner becoming strong, offset generating temperature will also become remarkably low and the blocking resistance of a toner will also fall remarkably further. Such a tendency is the same also in the toner of core shell structure. Therefore, it was difficult actually to obtain the toner with which these mercaptans are used for molecular weight adjustment, and it can be satisfied of mercaptans in respect of reduction of the melting characteristic or fixing temperature, preservability (blocking resistance), mobility, etc.

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[Translation done.]



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EFFECT OF THE INVENTION

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[Effect of the Invention]According to this invention, fixing temperature is low and Energy saving, printing, and improvement in the speed of a copy, It can respond to colorization etc. and, moreover, excels in preservability and mobility, and offset temperature is high, there is also no generating of a bad smell, and the toner for electrostatic charge image development which can form the picture of good image quality with high resolution is provided. The toner for electrostatic charge image development of this invention can be used with various image forming devices as a developer for developing an electrostatic latent image in a xerography, an electrostatic printing method, an electrostatic recording method, etc.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention]The purpose of this invention has low fixing temperature, and Energy saving, printing, and improvement in the speed of a copy, It can respond to colorization etc. and, moreover, in addition, excels in preservability and mobility, and offset temperature is high, there is also no generating of a bad smell, and it is in providing the toner for [ which can form the picture of good image quality with high resolution ] electrostatic charge image development, and its manufacturing method.

[0015]This invention persons found out that said purpose could be attained with the toner containing the binding resin obtained as a chain transfer agent using the third class thiol which has a structure specific at the time of a polymerization, as a result of inquiring wholeheartedly. Namely, it has at least two tertiary carbon atoms as a chain transfer agent at the time of the polymerization of binding resin, And if the third class thiol with 7-20 carbon atoms which have the structure which the sulfur atom coupled directly in at least one of tertiary carbon atoms of it is used, Comparatively little use can also fully lower the fixing temperature of a toner, and moreover can maintain offset generating temperature highly, a bad smell does not have it, either, further, it can excel in preservability and mobility and the toner for electrostatic charge image development which forms good image quality with high resolution can be obtained.

[0016]Conventionally, the third class thiol which has this specific structure is a technical field of a toner, and is the compound which was not used as a chain transfer agent or a regulator. In order that the third class thiol may participate in a chain transfer reaction, at least a part of the third class thiol used at the time of a polymerization will be combined as an alkylthio group in the generated polymer (binding resin) after a polymerization. This invention comes to be completed based on these knowledge.

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EXAMPLE

[Example]Although an example and a comparative example are given to below and this invention is explained more concretely, this invention is not limited only to these examples. A part and % are weight references as long as there is no notice especially. The measuring method of the physical properties in an example and a comparative example is as follows.

[0063](1) Particle diameter, volume average particle diameter (dv) of a particle-size-distribution polymer particle, and particle size distribution [Volume-average-particle-diameter (dv) / number average particle diameters (dn)] were measured by the multi-sizer (made by Beckman Coulter). Measurement by this multi-sizer was performed on measurement-particles number =100,000 piece conditions diameter =of aperture100micrometer, the medium = iso ton II, and concentration =10%.

[0064](2) If thick, it can measure with a multi-sizer or an electron microscope, but like an example and a comparative example, when thin, compute the thickness of the shell of the polymerization toner of shell thickness core shell structure using the following formulas.

$$x=r(1+s/100\rho)^{1/3}-r \quad (1)$$

However, the radius x of the mean particle diameter (volume particle diameter of a multi-sizer: micrometer) of the core-polymer particles before addition of the monomer for r:shell: Shell thickness (micrometer)

s: The number of addition parts of the monomer for shell (number of copies to 100 copies of monomers for cores)

rho: — density [ of a shell polymer ] (g/cm<sup>3</sup>); — usually — as rho= 1.0 — calculation.

[0065](3) Using the melting characteristic quantity-ized type flow tester (the Shimadzu make, CFT-500C), in accordance with the conventional method, the amount of plunger descent-temperature curve was created by the following measuring condition, and each temperature of the softening temperature (Ts) of a toner and the outflow starting point (Tfb) was searched for. Starting temperature: Every 35.0 \*\*, arrival temperature:250.0 \*\*, and time-between-measurements:2.5 \*\*/, heating-rate:3.0 \*\* /, and min, preheating time:300sec, and test

force:10.0kgf/cm<sup>2</sup>, nozzle hole diameter:0.50mm, nozzle 1.00 mm, and piston:1.0cm<sup>2</sup>. [ in length ]

[0066](4) The printer (printing speed = a part for 16-sheet/) of commercial one ingredient of nonmagnetic development system is used on the conditions of the printing test temperature of 23 \*\*, and 50% of relative humidity, The polymerization toner evaluated to the developer of this printer was put in, continuous printing was performed from the first stage, and printing density (initial printing density) was measured with the reflection density plan (made in Macbeth). Fogging on the photo conductor of a nonimage area was investigated with the whiteness degree plan (made by Nippon Denshoku) after the continuous printing of 20,000 sheets. Fogging made adhesive tape (Sumitomo 3M Scotch whisky mending tape 810-3-18) adhere to the nonimage area on a photo conductor, and was investigated. After making adhesive tape adhere to the nonimage area of the photo conductor before printing, it specifically removes, and this is stuck on a print form, and the whiteness degree A is measured. On the other hand, after making adhesive tape adhere to the nonimage area of the photo conductor after printing, it removes, and this is stuck on a print form, and the whiteness degree B is measured. Fogging (%) is computable

by A-B. Continuous printing was performed with printing density 5%.

[0067](5) The fixing examination was done using the printer converted so that the temperature of the fixing roll part of the printer (printing speed = a part for 16-sheet/) of one ingredient of nonmagnetic development system of fixing temperature marketing could be changed. The temperature of the fixing roll of a modified printer was changed, the fixing rate of the developer in each temperature was measured, and the fixing examination was done by asking for the relation of a temperature-fixing rate. The fixing rate was calculated from the ratio of the image concentration before and behind tape peeling operation of the black solid field in the examination paper which was neglected for more than 5 minutes in order to stabilize the temperature of a fixing roll, when changing temperature, and was printed with the modified printer after that. That is, if image concentration in front of ID and after tape exfoliation is carried out ID back, the fixing rate can compute the image concentration before tape exfoliation from a following formula.  
 fixing rate (%) = (after [ ID ] / before ID) x 100 — here, with tape peeling operation. Stick adhesive tape (Sumitomo 3M Scotch whisky mending tape 810-3-18) on the measured part of an examination paper, it is made to press and adhere in a constant pressure, and they are a series of operations of exfoliating adhesive tape in the direction which met paper with constant speed, after that. Image concentration was measured using the Macbeth reflection type image concentration measuring apparatus. In this fixing examination, fixing roll temperature applicable to 80% of a fixing rate was made into the fixing temperature of a developer.

[0068](6) Changed fixing temperature as well as hot offset generating temperature fixing temperature, black solid was made to print, and fixing roll temperature when offset occurred was made into hot offset generating temperature.

[0069](7) A fluid ratio (evaluation of mobility and preservability)

An opening puts from a top three sorts of sieves which are 150 micrometers, 75 micrometers, and 45 micrometers respectively on this order, and weighs precisely and carries the polymerization toner 4g measured on the top sieve. Subsequently, after vibrating three sorts of these piled-up sieves for 15 seconds on condition of the oscillating intensity graduation 4 using granular material measuring apparatus (the Hosokawa micron company make, trade name "powder tester"), the weight of the developer which remained on each sieve is measured. A fluid value is computed by putting each measured value into following formula \*\*, \*\*, and \*\*, and calculating the value of a, b, and c, next putting these values into formula \*\*. It measured 3 times per one sample, and the average value was calculated.

\*\* a = [(polymer weight (g) which remained in a 150-micrometer screen) / 4g] x 100  
 \*\* b = [(polymer weight (g) which remained in a 75-micrometer screen) / 4g] x 100 x 0.6  
 \*\* c = [(polymer weight (g) which remained in a 45-micrometer screen) / 4g] x 100 x 0.2  
 \*\* mobility (%) = 100 - (a+b+c)

The mobility in early stages of a developer ( $F_0$ ) is measured as mentioned above. On the other hand, after putting a developer into a container and saving for five days at 50 \*\*, mobility ( $F_1$ ) is measured in a similar manner. The fluid ratio ( $F_1/F_0$ ) was computed and it was considered as the index of preservability (blocking resistance) and mobility.

[0070](8) In the printing examination of the evaluation above-mentioned of a bad smell, organic-functions evaluation of the bad smell near a print paper exit was carried out by five healthy people, and the following standard estimated the bad smell.

C:3 or more persons as whom A:5 persons feel that a bad smell is, and B:1-2 persons who are not sense a bad smell sense a bad smell.

[0071][Example 1]

(1) The polymerization nature monomer for cores which consists of 80.5 copies of preparation styrene and 19.5 copies of n-butyl acrylate of a monomer composition (calculation Tg of the copolymer obtained = 55 \*\*), a polymethacrylic-acid-ester macro monomer (the Toagosei chemical industry company make.) A trade name "AA6", Tg = 94 \*\* 0.3 copy, 0.6 copy of divinylbenzene (55% of industrial use purity), 1.0 copy of 2,2,4,6,6-pentamethylheptane-4-thiol, 7.0 copies of carbon black (the Mitsubishi Chemical make, trade name "#25B"), 1.0 copy of charge controlling agent (the Hodogaya chemicals company make, trade name SUPIRON black TRH), a release agent [Shell and the product made by MDS, a trade name "FT-100"] After

stirring two copies with usual agitating equipment and mixing, uniform dispersion was carried out with the media type dispersion machine.

[0072](2) In the solution which dissolved 10.2 copies of magnesium chlorides (water-soluble polyvalent metallic salt) in 250 copies of ion exchange water at the preparation room temperatures of the drainage system carrier fluid object. It added gradually under stirring of the solution which dissolved 6.2 copies of sodium hydroxide (hydroxylation alkaline metal) in 50 copies of ion exchange water, and magnesium hydroxide colloid (metal hydroxide colloid of difficulty water solubility) dispersion liquid were prepared. When the particle size distribution of the generated above-mentioned colloid was measured with the micro track particle-size-distribution measuring instrument (made by Nikkiso Co., Ltd.),  $D_{50}$  (50% accumulated of number particle size distribution) was 0.35 micrometer, and  $D_{90}$  (90% accumulated of number particle size distribution) of particle diameter was 0.84 micrometer. In measurement by this micro track particle-size-distribution measuring instrument, it carried out on condition of medium = ion exchange water for measurement-range = 0.12–704 micrometer, and measuring time = 30 seconds.

[0073](3) Three copies of preparation methyl methacrylate (calculation  $T_g = 105$  \*\*) and 100 copies of water of the polymerization nature monomer for shell were micro-disperse-ization-processed with the ultrasonic emulsification machine, and the water dispersion of the polymerization nature monomer for shell was obtained.  $D_{90}$  was 1.6 micrometers, when the particle diameter of the drop of the polymerization nature monomer for shell in a water dispersion was applied by 3% of concentration into 1% hexametaphosphoric acid sodium solution and measured the obtained drop with the micro track particle-size-distribution measuring instrument.

[0074](4) In the magnesium hydroxide colloidal dispersion liquid obtained by the granulation stage above (2) at a room temperature. It agitates until it throws in the monomeric mixture obtained above (1) and a drop is stabilized, there — as a polymerization initiator — t-butylperoxy2-ethylhexanoate (the Nippon Oil & Fats Co., Ltd. make.) Trade name "par butyl O" Quantity shearing churning during 10 minutes was carried out at the number of rotations of 15,000 rpm after adding five copies using EBARAMAIRUDA (the Ebara Corp. make, trade name "MDN303 V type"), and the drop of the monomeric mixture was corned.

[0075](5) When the water dispersion of the monomeric mixture corned by the suspension polymerization process above (4) was put into the reactor equipped with stirring wings, a polymerization reaction was started at 95 \*\* and polymerization conversion reached to about 100%, it sampled and the particle diameter of the colored polymer particle (core) was measured. As a result, the volume average particle diameter of the core particle was 7.0 micrometers. Next, the polymerization nature monomer for shell and the water-soluble initiator which were prepared above (3) [The Wako Pure Chem make, trade name "VA-086"; 2,2' azobis [the 2-methyl- N -(2-hydroxy ethyl)- propionamide]] 0.3 copy was dissolved in 65 copies of distilled water, and it was put into the reactor. After continuing a polymerization for 8 hours, the reaction was suspended and the water dispersion of pH 9.5 polymer particle was obtained. Stirring the water dispersion of the polymer particle obtained by the above, pH of the system was set to about 5.0 with sulfuric acid, and acid cleaning (for 25 \*\* and 10 minutes) was performed. Subsequently, it filtered and dried, and after drying, wash water was sprinkled and backwashing by water was performed. Then, the oven (45 \*\*) performed 2 day-and-night desiccation, and the polymer particle was obtained.

[0076](6) To 100 copies of polymer particles of the core shell structure acquired by the developer above (5), 0.8 copy of silica (Degussa AG make; trade name "R972") with a mean particle diameter of 14 nm which carried out hydrophobing processing was added, it mixed to them using the Henschel mixer, and one ingredient of nonmagnetic developer was obtained. A result is shown in Table 1.

[0077][Example 2] In the preparation process of (1) monomer composition of Example 1, It carried out like Example 1 except having changed the addition of the divinylbenzene of a cross linking agent into 0.7 copy from 0.6 copy, and having changed the addition of the 2,2,4,6,6-

pentamethylheptane-4-thiol of a chain transfer agent into 2.0 copies from 1.0 copy, respectively. A result is shown in Table 1.

[0078][Example 3] In the preparation process of (1) monomer composition of Example 1, It carried out like Example 1 except having changed SUPIRON black TRH of the charge controlling agent into FCA626N (electrification control resin [ by FUJIKURA KASEI CO., LTD. ], and Mw= about 27,000, Mn= about 8,000, sulfonic group addition structural unit ratio 7-mol% of styrene acrylic ester resin). A result is shown in Table 1.

[0079][Example 4] In the preparation process of (1) monomer composition of Example 1, It carried out like Example 1 except having changed SUPIRON black TRH of the charge controlling agent into FCA626N, and having changed the "FT-100" 2 copy of the release agent into the dipentaerythritol hexa Millis Tait 10 copy, respectively. A result is shown in Table 1.

[0080][Comparative example 1] In the preparation process of (1) monomer composition of Example 1, it carried out like Example 1 except having changed the 2,2,4,6,6-pentamethylheptane-4-thiol of the chain transfer agent into t-dodecyl mercaptan. A result is shown in Table 1.

[0081][Comparative example 2] In the comparative example 1, it carried out like the comparative example 1 except having changed the addition of t-dodecyl mercaptan into 2.0 copies from 1.0 copy. A result is shown in Table 1.

[0082]

[Table 1]

	実 施 例				比 較 例	
	1	2	3	4	1	2
<b>コア (部)</b>						
スチレン	80.5	80.5	80.5	80.5	80.5	80.5
n-BA (*1)	19.5	19.5	19.5	19.5	19.5	19.5
マクロモノマー	0.3	0.3	0.3	0.3	0.3	0.3
架橋剤 (DVB) (*2)	0.6	0.7	0.6	0.6	0.6	0.7
着色剤 (CB) (*3)	7.0	7.0	7.0	7.0	7.0	7.0
帯電制御剤 (*4)	TRH	TRH	FCA	FCA	TRH	TRH
	1.0	1.0	1.0	1.0	1.0	1.0
離型剤 (*5)	FT-100	FT-100	FT-100	DPEHM	FT-100	FT-100
	2.0	2.0	2.0	10.0	2.0	2.0
連鎖移動剤						
PMHT (*6)	1.0	2.0	1.0	1.0	-	-
TDM (*7)	-	-	-	-	1.0	2.0
<b>シェル (部)</b>						
MMA (*8)	3.0	3.0	3.0	3.0	3.0	3.0
<b>重合トナー</b>						
体積平均粒径 (dv)	7.1	7.1	7.2	7.1	7.2	7.1
粒径分布 (dv/dn)	1.20	1.20	1.19	1.21	1.20	1.21
シェル厚 (μm)	0.04	0.04	0.04	0.04	0.04	0.04
溶融特性						
Ts (°C) (*9)	63.4	64.0	65.1	64.5	62.7	60.5
Tfb (°C) (*10)	132	148	138	135	125	110
<b>現像剤特性</b>						
印字濃度	1.42	1.45	1.43	1.45	1.43	1.45
2万枚印字後						
カブリ	1.2	0.8	1.3	1.5	1.5	1.4
定着温度 (°C)	135	135	140	125	165	130
ホットオフセット						
発生温度 (°C)	220	220	220	220	220	150
保存 (50°C/5日) 前						
後の流動性比	0.98	0.95	1.16	0.99	0.97	0.35
印字臭気	A	A	A	A	B	C

[0083]( Footnote)

(\*1) n-BA:n-butyl acrylate (\*2) DVB : divinylbenzene (55% of purity)

CB:carbon black (\*4) charge controlling agent TRH : (\*3) The Hodogaya chemicals company make, SUPIRON Black TRHFCA: The FUJIKURA KASEI CO., LTD. make, electrification control resin FCA626N (\*5) release agent FT-100 : Shell and the product made by MDS, Fischer Tropsch wax DPEHM:dipentaerythritol hexa Millis Tait (\*6) — PMHT:2,2,4,6,6-pentamethylheptane-4-thiol (\*7) TDM:t-dodecyl mercaptan (\*8) MMA:methyl methacrylate. (\*9) Ts: — softening temperature (\*10) Tfb: of a toner — the outflow starting point of a toner [0084] By using the specific third class thiol as a chain transfer agent so that clearly from the result of Table 1 (Examples 1-4), Fixing temperature is reduced, moreover, offset temperature is maintained to an elevated temperature, in addition, there is no bad smell, and the toner for electrostatic charge image development which can form a high-definition picture can be obtained. On the other hand, if t-dodecyl mercaptan which is a general-purpose chain transfer agent is used, When there are few the additions (comparative example 1), fixing temperature cannot be lowered, but when there are many additions (comparative example 2), the offset temperature of that to which fixing temperature can be reduced falls remarkably, moreover the bad smell at the time of printing becomes severe, and preservability also falls.

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[Translation done.]



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(54) 【発明の名称】 静電荷像現像用トナー及びその製造方法

(57) 【要約】

【課題】 定着温度が低く、省エネルギー化、印字及び複写の高速化、カラー化などに対応することができ、しかもなお、保存性と流動性に優れ、オフセット温度が高く、臭気の発生もなく、高解像度で良好な画質の画像を形成することが可能な静電荷像現像用トナーを提供すること。

【解決手段】 少なくとも結着樹脂及び着色剤を含有する着色重合体粒子を含む静電荷像現像用トナーにおいて、該結着樹脂が、少なくとも 2 個の第三級炭素原子を有し、かつ、そのうちの少なくとも 1 個の第三級炭素原子には硫黄原子が直接結合した構造を持つ炭素原子数 7 ～ 2 0 のアルキルチオ基が結合した重合体であることを特徴とする静電荷像現像用トナー、及びその製造方法。

## 【特許請求の範囲】

【請求項1】 少なくとも結着樹脂及び着色剤を含有する着色重合体粒子を含む静電荷像現像用トナーにおいて、該結着樹脂が、少なくとも2個の第三級炭素原子を有し、かつ、そのうちの少なくとも1個の第三級炭素原子には硫黄原子が直接結合した構造を持つ炭素原子数7～20のアルキルチオ基が結合した重合体であることを特徴とする静電荷像現像用トナー。

【請求項2】 フローテスターで測定したトナーの軟化点(Ts)が62～67℃で、流出開始点(Tfb)が110℃以上である請求項1記載の静電荷像現像用トナー。

【請求項3】 分散安定剤を含有する水系分散媒体中で、少なくとも重合性単量体及び着色剤を含有する単量体混合物を懸濁重合して着色重合体粒子を生成させる工程を含む静電荷像現像用トナーの製造方法において、該単量体混合物中に、連鎖移動剤として、少なくとも2個の第三級炭素原子を有し、かつ、そのうちの少なくとも1個の第三級炭素原子には硫黄原子が直接結合した構造を持つ炭素原子数7～20の第三級チオールを含有させることを特徴とする静電荷像現像用トナーの製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、電子写真法、静電記録法、静電印刷法などにおいて形成される静電潜像の現像に用いられる静電荷像現像用トナー及びその製造方法に関する。

## 【0002】

【従来の技術】電子写真法、静電記録法、静電印刷法などにおいて、感光体上に形成された静電潜像を可視化するための現像剤として、トナー（静電荷像現像用トナー）が用いられている。トナーは、結着樹脂、着色剤、帯電制御剤、離型剤などを含有する着色粒子である。トナーの製造方法は、粉砕法と重合法に大別される。粉砕法は、結着樹脂や着色剤などの各成分を溶解混練し、次いで、粉砕し、分級してトナー（粉砕法トナー）を製造する方法である。粉砕法では、結着樹脂として粉砕されやすい脆性のある材質のものを使用する必要があるため、粉砕工程で多量の微粉末が発生する。これらの微粉末は、分級により除去しなければならないが、工程が煩雑で、しかも歩留りが低くなる。さらに、粉砕法トナーは、結着樹脂が脆い材質であるため、複写機などの装置内で使用時に微粉化され、その結果、画質が低下する。

【0003】一方、重合法は、分散安定剤を含有する水系分散媒体中で、重合性単量体、着色剤、帯電制御剤、離型剤などを含有する単量体混合物を懸濁重合することにより、着色剤などを含有する重合体粒子を生成させる方法である。重合法では、得られた着色重合体粒子をトナー（重合トナー）として使用することができる。このように、重合法では、粉砕工程を必要としないため、重

合性単量体として、粉砕され難い重合体を形成し得る材料を選択することができる。重合トナーは、実質的に球形であるため、流動性に優れ、しかも粒径分布が粉砕法トナーと比較して格段にシャープである。

【0004】静電荷像現像用トナーには、精細で高濃度の優れた画質の画像を形成することができ、温度や湿度などの環境の変化によっても画質が劣化せず、しかも連続印字や連続複写が可能であることなどが要求されている。これらの特性に加えて、最近、静電荷像現像用トナーには、省エネルギーに寄与できること、印字及び複写の高速化に対応できること、フルカラー化に対応できることなどが求められている。そのために、静電荷像現像用トナーには、高画質を維持し、保存性を損なうことなく、しかもなお、定着温度の低下などの定着性を改善することが求められている。

【0005】具体的には、最近、静電荷像現像用トナーが使用される電子写真方式の複写機やプリンター等の画像形成装置において、消費電力の低減化が図られている。電子写真方式の中でも特にエネルギーを消費する工程は、感光体上のトナー像を紙などの転写材上に転写した後、定着するための定着工程である。一般に、定着工程では、トナー像を転写材上に定着させるために、150℃以上に加熱した定着ロールや定着ベルトが使用され、そのエネルギー源として電気が使われている。この定着温度を下げることで、省エネルギーの観点から求められている。

【0006】また、最近、印字速度や複写速度の高速化が求められている。特に、画像形成装置の複合化やパーソナルコンピュータのネットワーク化が進む中で、高速印字や高速複写に対する要求は益々強くなっている。そのため、高速プリンターや高速複写機においては、定着時間の短縮化が必要になっている。

【0007】静電荷像現像用トナーの設計において、こうした画像形成装置からの要求に応える手法として、結着樹脂のガラス転移温度(Tg)を低下させる方法がある。しかし、結着樹脂のTgを低下させると、トナーの保存中あるいは現像装置のトナーボックス中で、トナー粒子が互いにブロッキングを起こして凝集体となり、いわゆる保存性の悪いトナーとなってしまう。

【0008】さらに、最近では、電子写真方式によるカラー印字やカラー複写技術が開発されている。カラー印字やカラー複写を行うには、感光体上の静電潜像を、通常、3ないし4色のカラートナーを用いて現像し、転写材上に一度にあるいは順次転写し、しかる後、定着している。このため、白黒画像に比べて定着するトナーの層厚が厚くなる。また、混色により所定の色調に発色させるには、定着時に、重なった複数のカラートナーを均一に溶解させることが必要である。

【0009】そのために、カラートナーでは、定着温度付近での溶解粘度を従来のものに比べて低く設計して、

溶融しやすくする必要がある。トナーの溶融粘度を低くする手法としては、従来のトナーに比べて、結着樹脂の分子量を低くしたり、T<sub>g</sub>を下げるなどの方法がある。しかし、いずれの方法でも、ブロッキングを起しやすく、保存性の悪いトナーになってしまう。このように、省エネルギー化、印字や複写の高速化、カラー化に対応するトナーの改質手法を採用すると、トナーの保存性が低下する。

【0010】従来、静電荷像現像用トナーの定着温度を下げ、同時に、耐ブロッキング性を向上させる手法として、コア・シェル構造を有するトナーが提案されている。具体的には、少なくとも結着樹脂と着色剤を含有する着色粒子をコアとし、該コアをT<sub>g</sub>が高い樹脂で被覆した構造のトナー粒子（カプセルトナーともいう）を形成する方法である。重合法では、少なくとも重合性単量体及び着色剤を含有する重合性単量体混合物を懸濁重合して着色重合体粒子を生成させ、次いで、該着色重合体粒子の存在下に、該着色重合体粒子を構成する重合体成分のT<sub>g</sub>よりも高いT<sub>g</sub>の重合体を生成することができる重合性単量体を重合させることにより、コア・シェル構造の重合体粒子を生成させる方法が知られている。この手法を採用すると、低T<sub>g</sub>の着色重合体粒子（コア）の周囲を高T<sub>g</sub>の薄い重合体層（シェル）で被覆した構造の重合体粒子を得ることができる。

【0011】このようなコア・シェル構造のトナーは、コアを構成する結着樹脂のT<sub>g</sub>を充分に低くすることにより、定着温度を下げるできるとともに、高T<sub>g</sub>の重合体層からなるシェルにより、トナー同士のブロッキングを抑制することができる。しかし、このようなコア・シェル構造のトナーであっても、定着温度を下げるために、コアを構成する結着樹脂のT<sub>g</sub>を下げると、オフセットが発生する温度も低くなるため、高画質を得ることは困難であった。

【0012】従来、結着樹脂の分子量を調整するために、重合性単量体を $\alpha$ -ブチルメルカプタンなどの連鎖移動剤の存在下に重合する方法が知られている（例えば、特開平11-38674号公報の段落番号【0032】）。連鎖移動剤を用いて結着樹脂を製造すると、結着樹脂の分子量を低くすることができ、低T<sub>g</sub>化も容易であるため、トナーの溶融特性の向上や定着温度の低減が期待される。

【0013】しかしながら、従来からトナーの技術分野で典型的な連鎖移動剤として提案されている $\alpha$ -ブチルメルカプタンや $n$ -ブチルメルカプタンなどのメルカプタン類は、結着樹脂中に残留するため、トナーが刺激臭を発生するという問題があった。これらのメルカプタン類の使用量を少なくすると、トナーの臭気を抑制することができるものの、トナーの定着温度を充分に下げることができない。一方、これらのメルカプタン類の使用量を多くすると、トナーの定着温度を充分に下げるこ

とができるものの、刺激臭が強くなることに加えて、オフセット発生温度も著しく低くなり、さらには、トナーの耐ブロッキング性も著しく低下する。このような傾向は、コア・シェル構造のトナーにおいても同様である。したがって、これらのメルカプタン類を分子量調整のために用いて、溶融特性や定着温度の低減、保存性（耐ブロッキング性）、流動性などの点で満足できるトナーを得ることは、実際には、困難であった。

【0014】

【発明が解決しようとする課題】本発明の目的は、定着温度が低く、省エネルギー化、印字及び複写の高速化、カラー化などに対応することができ、しかもなお、保存性と流動性に優れ、オフセット温度が高く、臭気の発生もなく、高解像度で良好な画質の画像を形成することが可能な静電荷像現像用トナーとその製造方法を提供することにある。

【0015】本発明者らは、鋭意研究した結果、重合時に特定の構造を有する第三級チオールを連鎖移動剤として使用して得られた結着樹脂を含有するトナーにより、前記目的を達成できることを見いだした。すなわち、結着樹脂の重合時に、連鎖移動剤として、少なくとも2個の第三級炭素原子を有し、かつ、そのうちの少なくとも1個の第三級炭素原子には硫黄原子が直接結合した構造を持つ炭素原子数7～20の第三級チオールを用いると、比較的少量の使用でも、トナーの定着温度を充分に下げることができ、しかも、オフセット発生温度を高く維持することができ、臭気もなく、さらには、保存性と流動性に優れ、高解像度で良好な画質を形成する静電荷像現像用トナーを得ることができる。

【0016】この特定の構造を有する第三級チオールは、従来、トナーの技術分野で、連鎖移動剤または分子量調整剤として使用されていなかった化合物である。第三級チオールは、連鎖移動反応に関与するため、重合時に使用した第三級チオールの少なくとも一部は、重合後、生成した重合体（結着樹脂）中にアルキルチオ基として結合することになる。本発明は、これらの知見に基づいて完成するに至ったものである。

【0017】

【課題を解決するための手段】本発明によれば、少なくとも結着樹脂及び着色剤を含有する着色重合体粒子を含む静電荷像現像用トナーにおいて、該結着樹脂が、少なくとも2個の第三級炭素原子を有し、かつ、そのうちの少なくとも1個の第三級炭素原子には硫黄原子が直接結合した構造を持つ炭素原子数7～20のアルキルチオ基が結合した重合体であることを特徴とする静電荷像現像用トナーが提供される。

【0018】また、本発明によれば、分散安定剤を含有する水系分散媒体中で、少なくとも重合性単量体及び着色剤を含有する単量体混合物を懸濁重合して着色重合体粒子を生成させる工程を含む静電荷像現像用トナーの製

造方法において、該単量体混合物中に、連鎖移動剤として、少なくとも2個の第三級炭素原子を有し、かつ、そのうちの少なくとも1個の第三級炭素原子には硫黄原子が直接結合した構造を持つ炭素原子数7~20の第三級チオールを含有させることを特徴とする静電荷像現像用トナーの製造方法が提供される。

【0019】

【発明の実施の形態】1. 静電荷像現像用トナーの製造方法

本発明の静電荷像現像用トナーの製造方法は、特に限定されないが、重合法を採用することが好ましい。重合法による重合トナーは、通常、分散安定剤を含有する水系分散媒体中で、少なくとも重合性単量体及び着色剤を含有する単量体混合物を懸濁重合することにより、着色剤などを含有する重合体粒子（着色重合体粒子）として得ることができる。本発明では、単量体混合物に、重合性単量体と着色剤に加えて、連鎖移動剤として特定の第三級チオールを含有させるが、必要に応じて、架橋性単量体、帯電制御剤、離型剤、その他の分子量調整剤、マクロモノマー、重合開始剤、その他の各種添加剤を含有させることができる。

【0020】コア・シェル構造の重合トナーは、分散安定剤を含有する水系分散媒体中で、少なくとも重合性単量体及び着色剤を含有する単量体混合物を懸濁重合して着色重合体粒子を生成させ、次いで、該着色重合体粒子の存在下に、該着色重合体粒子を構成する重合体成分のガラス転移温度よりも高いガラス転移温度の重合体を生成することができる重合性単量体を重合させることにより得ることができる。本発明では、コアを形成する単量体混合物に、特定の第三級チオールを含有させる。したがって、本発明は、このようなコア・シェル構造の重合トナーとその製造方法も包含している。

【0021】(1) 重合性単量体

重合性単量体としては、モノビニル系単量体が好ましい。具体的には、スチレン、ビニルトルエン、 $\alpha$ -メチルスチレン等のスチレン系単量体；アクリル酸、メタクリル酸；アクリル酸メチル、アクリル酸エチル、アクリル酸プロピル、アクリル酸ブチル、アクリル酸2-エチルヘキシル、アクリル酸ジメチルアミノエチル、メタクリル酸メチル、メタクリル酸エチル、メタクリル酸プロピル、メタクリル酸ブチル、メタクリル酸2-エチルヘキシル、メタクリル酸ジメチルアミノエチル、アクリロニトリル、メタクリロニトリル、アクリルアミド、メタクリルアミド等のアクリル酸またはメタクリル酸の誘導体；エチレン、プロピレン、ブチレン等のエチレン性不飽和モノオレフィン；塩化ビニル、塩化ビニリデン、フッ化ビニル等のハロゲン化ビニル；酢酸ビニル、プロピオン酸ビニル等のビニルエステル；ビニルメチルエーテル、ビニルエチルエーテル等のビニルエーテル；ビニルメチルケトン、メチルイソプロペニルケトン等のビニル

ケトン；2-ビニルピリジン、4-ビニルピリジン、N-ビニルピロリドン等の含窒素ビニル化合物；などが挙げられる。モノビニル系単量体は、それぞれ単独で、あるいは複数の単量体を組み合わせて用いることができる。モノビニル系単量体のうち、スチレン系単量体と（メタ）アクリル酸の誘導体とを併用するのが好適である。

【0022】(2) 架橋性単量体及び架橋性重合体

重合性単量体と共に架橋性単量体及び／または架橋性重合体を用いると、ホットオフセット改善に有効である。架橋性単量体は、2以上の重合可能な炭素-炭素不飽和二重結合を有する単量体である。具体的には、ジビニルベンゼン、ジビニルナフタレン、これらの誘導体等の芳香族ジビニル化合物；エチレングリコールジメタクリレート、ジエチレングリコールジメタクリレート等のジエチレン性不飽和カルボン酸エステル；1,4-ブタンジオール、1,9-ノナンジオール等の脂肪族両末端アルコール由来の（メタ）アクリレート；N,N-ジビニルアニリン、ジビニルエーテル等のジビニル化合物；3個以上のビニル基を有する化合物；などを挙げることができる。架橋性重合体としては、分子内に2個以上の水酸基を有するポリエチレンやポリプロピレン、ポリエステルやポリシロキサン由来の（メタ）アクリレート等を挙げることができる。これらの架橋性単量体及び架橋性重合体は、それぞれ単独で、あるいは2種以上を組み合わせ用いることができる。架橋性単量体及び／または架橋性重合体は、重合性単量体100重量部に対して、通常10重量部以下、好ましくは0.01~5重量部、より好ましくは0.1~2重量部の割合で使用される。

【0023】(3) マクロモノマー

重合性単量体と共にマクロモノマーを用いると、保存性やオフセット防止性と低温定着性とのバランスを良くすることができる。マクロモノマーは、分子鎖の末端に重合可能な官能基（例えば、炭素-炭素二重結合のような不飽和基）を有する比較的長い線状分子である。マクロモノマーとしては、数平均分子量が通常1,000~30,000のオリゴマーまたはポリマーが好ましい。数平均分子量が小さいマクロモノマーを用いると、トナー粒子の表面部分が柔らかくなり、保存性が低下する。逆に、数平均分子量が大きいマクロモノマーを用いると、マクロモノマーの溶解性が悪く、トナーの定着性が低下する。

【0024】マクロモノマーの具体例としては、スチレン、スチレン誘導体、メタクリル酸エステル、アクリル酸エステル、アクリロニトリル、メタクリロニトリル等を単独でまたは2種以上を重合して得られる重合体、ポリシロキサン骨格を有するマクロモノマーなどが挙げられる。マクロモノマーの中でも、結着樹脂のガラス転移温度より高いガラス転移温度を有する重合体为好ましく、特にスチレンとメタクリル酸エステル及び／または

アクリル酸エステルとの共重合体マクロモノマーやポリメタクリル酸エステルマクロモノマーが好適である。マクロモノマーを使用する場合、その配合割合は、重合性単量体100重量部に対して、通常0.01~10重量部、好ましくは0.03~5重量部、より好ましくは0.05~1重量部である。マクロモノマーの使用割合が大きすぎると、定着性が低下する傾向を示す。

#### 【0025】(4) 着色剤

着色剤としては、カーボンブラックやチタンホワイトなどのトナーの分野で用いられている各種顔料及び染料を使用することができる。黒色着色剤としては、カーボンブラック、ニグロシンベースの染料顔料類；コバルト、ニッケル、四三酸化鉄、酸化鉄マンガン、酸化鉄亜鉛、酸化鉄ニッケル等の磁性粒子；などを挙げることができる。カーボンブラックを用いる場合、一次粒径が20~40nmであるものを用いると良好な画質が得られ、また、トナーの環境への安全性も高まるので好ましい。

【0026】カラートナー用着色剤としては、イエロー着色剤、マゼンタ着色剤、シアン着色剤などを使用することができる。イエロー着色剤としては、例えば、C. 1. ビグメントイエロー3、12、13、14、15、17、62、65、73、83、90、93、97、120、138、155、180、181；ネフトールイエローS、ハンザイエローG、C. 1. バットイエロー等が挙げられる。

【0027】マゼンタ着色剤としては、アゾ系顔料、縮合多環系顔料等が挙げられ、より具体的には、例えば、C. 1. ビグメントレッド48、57、58、60、63、64、68、81、83、87、88、89、90、112、114、122、123、144、146、149、163、170、184、185、187、202、206、207、209、251；C. 1. ビグメントバイオレット19等が挙げられる。

【0028】シアン着色剤としては、銅フタロシアニン化合物及びその誘導体、アントラキノン化合物等が挙げられ、より具体的には、例えば、C. 1. ビグメントブルー2、3、6、15、15:1、15:2、15:3、15:4、16、17、60；フタロシアニンブルー、C. 1. バットブルー、C. 1. アシッドブルーなどが挙げられる。該着色剤は、結着樹脂または結着樹脂を形成する重合性単量体100重量部に対して、通常0.1~50重量部、好ましくは1~20重量部の割合で用いられる。

#### 【0029】(5) 連鎖移動剤

本発明では、連鎖移動剤として、特定の第三級チオールを使用する。本発明で使用する第三級チオールは、少なくとも2個の第三級炭素原子を有し、かつ、そのうちの少なくとも1個の第三級炭素原子には硫黄原子が直接結合した構造を持つ炭素原子数7~20の第三級チオールである。第三級炭素原子とは、水素原子が一つも結合し

ていない炭素原子を意味する。この第三級炭素原子には、メチル基などのアルキル基、またはアルキル基とSH基が結合している。第三級チオールの炭素原子数は、合成の容易さや作用効果の観点から、好ましくは9~16である。第三級炭素原子の数は、好ましくは3個である。SH基の結合数は、好ましくは1個である。

【0030】本発明で使用する第三級チオールとしては、例えば、2, 5, 5-トリメチルヘキサノ-2-チオール、2, 2, 4, 6, 6-ペンタメチルヘプタノ-4-チオール、2, 2, 4, 4, 6-ペンタメチルヘプタノ-6-チオール、2, 2, 4, 6, 6, 8, 8-ヘプタメチルノナン-4-チオール、2, 2, 5, 8, 8-ペンタメチルノナン-5-チオール、2, 2, 5, 5, 6, 8, 8-ヘプタメチルノナン-6-チオールなどが挙げられる。

【0031】連鎖移動剤の第三級チオールの使用割合は、重合性単量体100重量部に対して、通常、0.05~4重量部、好ましくは0.1~3重量部、より好ましくは0.5~2重量部である。第三級チオールの使用割合が小さすぎると、定着温度の低減効果が小さくなり、大きすぎると、保存性が低下傾向を示す。

【0032】本発明においては、第三級チオール以外に、その他の連鎖移動剤（分子量調整剤）を必要に応じて併用することができる。その他の連鎖移動剤としては、例えば、n-オクチルメルカブタン、n-ドデシルメルカブタン、t-ドデシルメルカブタン、n-ヘキサデシルメルカブタン、n-テトラデシルメルカブタン、2, 2, 4, 6, 6-ペンタメチルヘプタノ-4-メチレンチオール、2, 4, 6-トリメチルノナン-4-チオール、トリデシルメルカブタンテトラデシルメルカブタン、ヘキサデシルメルカブタンなどのメルカブタン類；ジメチルキサントゲンジスルフィド、ジエチルキサントゲンジスルフィド、ジイソプロピルキサントゲンジスルフィドなどのキサントゲンジスルフィド類；テトラメチルチウラムジスルフィド、テトラエチルチウラムジスルフィド、テトラブチルチウラムジスルフィドなどのチウラムジスルフィド類；四塩化炭素、臭化エチレンなどのハロゲン化炭化水素類；ペンタフェニルエタンなどの炭化水素類；アクロレイン、メタクロレイン等の $\alpha$ ,  $\beta$ -不飽和アルデヒド類；アリルアルコール；2-エチルヘキシルチオグリコレート；テルビノーレン、 $\alpha$ -テルビネン、 $\beta$ -テルビネン、 $\gamma$ -テルビネン、ジベンテン等のテルペン類；2-4-ジフェニル-4-メチル-1-ペンテン等の $\alpha$ -メチルスチレンダイマー；2, 5-ジヒドロフランなどが挙げられる。その他の連鎖移動剤は、必ずしも使用する必要はなく、また、使用する場合でも、臭気の発生やオフセット温度の低下、保存性の低下などのないように、少量の範囲で使用される。

#### 【0033】(6) 滑剤・分散助剤

着色剤のトナー粒子中への均一分散等を目的として、オ

レイン酸、ステアリン酸等の脂肪酸、脂肪酸とNa、K、Ca、Mg、Zn等の金属とからなる脂肪酸金属塩などの滑剤；シラン系またはチタン系カップリング剤等の分散助剤；などを使用してもよい。このような滑剤や分散剤は、着色剤の重量を基準として、通常1/1000～1/1程度の割合で使用される。

#### 【0034】(7) 帯電制御剤

トナーの帯電性を向上させるために、各種の正帯電性または負帯電性の帯電制御剤を単量体組成物中に含有させることが好ましい。帯電制御剤としては、例えば、ポントロンN01（オリエント化学社製）、ニグロシンベースEX（オリエント化学社製）、スピロブラックTRH（保土ケ谷化学社製）、T-77（保土ケ谷化学社製）、ポントロンS-34（オリエント化学社製）、ポントロンE-81（オリエント化学社製）、ポントロンE-84（オリエント化学社製）、ポントロンE-89（オリエント化学社製）、ポントロンF-21（オリエント化学社製）、COPY CHARGE NX（クラリアント社製）、COPY CHARGE NEG（クラリアント社製）、TNS-4-1（保土ケ谷化学社製）、TNS-4-2（保土ケ谷化学社製）、LR-147（日本カーリット社製）などの帯電制御剤；特開平11-15192号公報、特開平3-175456号公報、特開平3-243954号公報などに記載の4級アンモニウム（塩）基含有共重合体、特開平3-243954号公報、特開平1-217464号公報、特開平3-15858号公報などに記載のスルホン酸（塩）基含有共重合体等の帯電制御樹脂；等を用いることができる。帯電制御剤は、結着樹脂または結着樹脂を形成する重合性単量体100重量部に対して、通常0.01～10重量部、好ましくは0.1～7重量部の割合で用いられる。

#### 【0035】(8) 低軟化点物質

トナーの定着温度を下げたり、離型性を高めるなどのために、低軟化点物質を用いることが好ましい。低軟化点物質は、単量体混合物中に添加して、生成する重合トナー中に含有させる。重合トナーがコア・シェル構造を有するものである場合には、低軟化点物質は、コアとなる着色重合体粒子中に含有させる。

【0036】低軟化点物質は、重合性単量体の主成分として汎用のスチレン単量体に室温で可溶性のものであることが好ましい。このような低軟化点物質としては、3官能以上のアルコールとカルボン酸とからなる多官能エステル化合物や、炭素数15以上のアルコールとカルボン酸とからなる芳香族カルボン酸エステル化合物が好ましい。低軟化点物質がスチレン単量体に非可溶性のものである場合には、重合性単量体組成物を調製する工程で、低軟化点物質の熔融温度以上の温度に加熱して分散させる必要があるが、このようにして分散させても、重合工程で生成する重合トナー表面にブリードしやすいので、好ましくない。

【0037】3官能以上のアルコールとしては、グリセリン、ペンタエリスリトール、ジペンタエリスリトール、ペンタグリセロールなどの脂肪族アルコール類；フロログリシトール、クエルシトール、イノシトールなどの脂環式アルコール類；トリス（ヒドロキシメチル）ベンゼンなどの芳香族アルコール類；D-エリトース、L-アラビノース、D-マンノース、D-ガラクトース、D-フルクトース、L-ラムノース、サッカロース、マルトース、ラクトースなどの糖類；エリトリット、D-トレイット、L-アラビット、アドニット、キシリットなどの糖アルコール類；などを挙げることができる。これらのうち、ペンタエリスリトール、ジペンタエリスリトールが好適である。

【0038】炭素原子数が15以上のアルコールの具体例としては、ペンタデシルアルコール、セチルアルコール、ヘプタデシルアルコール、ステアシルアルコール、ノナデシルアルコール、エイコシルアルコール、ベヘニルアルコール、セリルアルコール、メシリルアルコールなどが挙げられる。

【0039】カルボン酸としては、酢酸、酪酸、カプロン酸、エナント酸、カプリル酸、ベラルゴン酸、カプリン酸、ウンデカン酸、ラウリン酸、ミリスチン酸、ステアリン酸、マルガリン酸、アラキジン酸、セロチン酸、メリキシン酸、エリカ酸、ブラシジン酸、ソルビン酸、リノール酸、リノレン酸、ベヘニル酸、テトロール酸、キシメニン酸などの脂肪族カルボン酸類；シクロヘキサンカルボン酸、ヘキサヒドロイソフタル酸、ヘキサヒドロテレフタル酸、3,4,5,6-テトラヒドロフタル酸などの脂環式カルボン酸類；安息香酸、トルイル酸、クミン酸、フタル酸、イソフタル酸、テレフタル酸、トリメシン酸、トリメリット酸、ヘミメリット酸などの芳香族カルボン酸類；等を挙げることができる。これらの中でも、炭素原子数が通常10～30個、好ましくは13～25個のカルボン酸、特に該炭素原子数の脂肪族カルボン酸類や、カルボキシル基が2以上の芳香族カルボン酸が好適である。

【0040】多官能エステル化合物は、3官能以上のアルコールの各水酸基と結合する複数のカルボン酸が、それぞれ異なるものであっても、同じものであってもよいが、好適には、複数のカルボン酸中の炭素原子数の最大値と最小値との差が9以下、好ましくは5以下のものである。具体的には、ペンタエリスリトールテトラミリスレート、ペンタエリスリトールテトララウレート、ジペンタエリスリトールヘキサミリスレートとグリセロールトリアラキン酸などを挙げることができる。

【0041】低軟化点物質としては、示差走査熱量計（DSC）により測定されるDSC曲線において、昇温時の吸熱ピーク温度が通常30～200℃、好ましくは50～180℃の範囲内にあるものが望ましい。より具体的に、吸熱ピーク温度が60～160℃の範囲内にあ

るペンタエリスリトールエステル、50～80℃の範囲内にあるジペンタエリスリトールエステルなどの多官能エステル化合物や芳香族カルボン酸エステル化合物が挙げられる。これらの多官能エステル化合物芳香族カルボン酸エステル化合物は、低温定着性と離型性とのバランスの面で特に好ましい。

【0042】とりわけ、分子量が600以上で、25℃のスチレン100gに対する溶解量(g/100g ST; 25℃)が5g以上、より好ましくは10g以上、かつ、酸価が10mg/KOH以下である多官能エステル化合物が好ましい。特にこれらの物性を有するジペンタエリスリトールエステルは、定着温度の低下に著効を示す。吸熱ピーク温度は、ASTM-D-3418-82によって測定した値である。酸価は、JIS-K-1557-1970に準じて測定した値である。

【0043】芳香族カルボン酸エステル化合物の場合、35℃で測定したスチレン100gに対する溶解量(g/100g ST; 35℃)は、好ましくは5g以上、より好ましくは10g以上、特に好ましくは15g以上である。芳香族カルボン酸エステル化合物の酸価は、好ましくは2mg KOH/g以下、より好ましくは1.5mg KOH/g以下、特に好ましくは1.3mg KOH/g以下であり、多くの場合、1.0mg KOH/g以下、0.1mg KOH/g以上である。低軟化点物質は、重合性単量体100重量部に対して、通常、0.1～20重量部、好ましくは1～15重量部の割合で使用される。

#### 【0044】(9) 離型剤

多官能エステル化合物などの低軟化点物質は、離型剤としても作用するため、これらを使用する場合には、その他の離型剤の使用は必要ないけれども、所望により、オフセット防止などの目的で、その他の各種離型剤を含有させることができる。離型剤としては、例えば、低分子量ポリエチレン、低分子量ポリプロピレン、低分子量ポリブチレンなどの低分子量ポリオレフィンワックス類；分子末端酸化低分子量ポリプロピレン、分子末端をエポキシ基に置換した低分子量末端変性ポリプロピレン、及びこれらと低分子量ポリエチレンのブロックポリマー、分子末端酸化低分子量ポリエチレン、分子末端をエポキシ基に置換した低分子量ポリエチレン、及びこれらと低分子量ポリプロピレンのブロックポリマーなどの末端変性ポリオレフィンワックス類；キャンデリラ、カルナウバ、ライス、木ロウ、ホホバなどの植物系天然ワックス；パラフィン、マイクロクリスタリン、ペトロラクタムなどの石油系ワックス及びその変性ワックス；モンタン、セレシン、オゾケライト等の鉱物系ワックス；フィッシュアトロブシュワックスなどの合成ワックス；これらの混合物等が例示される。これらの離型剤は、結着樹脂または結着樹脂を形成する重合性単量体100重量部に対して、0.1～20重量部（更には1～15重量

部)用いることが好ましい。

#### 【0045】(10) 重合開始剤

重合開始剤としては、ラジカル重合開始剤が好適に用いられる。具体的には、過硫酸カリウム、過硫酸アンモニウム等の過硫酸塩；4, 4'-アゾビス(4-シアノ吉草酸)、2, 2'-アゾビス(2-アミノプロパン)二塩酸塩、2, 2'-アゾビス-2-メチル-N-1, 1-ビス(ヒドロキシメチル)-2-ヒドロキシエチルプロピオアミド、2, 2'-アゾビス(2, 4-ジメチルパレロニトリル)、2, 2'-アゾビスイソブチロニトリル、1, 1'-アゾビス(1-シクロヘキサンカルボニトリル)等のアゾ化合物；イソブチルパーオキサイド、2, 4-ジクロロベンゾイルパーオキサイド、3, 5, 5'-トリメチルヘキサノイルパーオキサイド等のジアシルパーオキサイド系；ビス(4-*t*-ブチルシクロヘキシル)パーオキシジカーボネート、ジ-*n*-プロピルパーオキシジカーボネート、ジ-イソプロピルパーオキシジカーボネート、ジ-2-エトキシエチルパーオキシジカーボネート、ジ(2-エチルエチルパーオキシ)ジカーボネート、ジ-メトキシブチルパーオキシジカーボネート、ジ(3-メチル-3-メトキシブチルパーオキシ)ジカーボネート等のパーオキシジカーボネート類；( $\alpha$ ,  $\alpha$ -ビス-ネオデカノイルパーオキシ)ジイソプロピルベンゼン、クミルパーオキシネオデカノエート、1, 1', 3, 3'-テトラメチルブチルパーオキシネオデカノエート、1-シクロヘキシル-1-メチルエチルパーオキシネオデカノエート、*t*-ヘキシルパーオキシネオデカノエート、*t*-ブチルパーオキシネオデカノエート、*t*-ヘキシルパーオキシビバレート、*t*-ブチルパーオキシビバレート、メチルエチルパーオキシド、ジ-*t*-ブチルパーオキシド、アセチルパーオキシド、ジクミルパーオキシド、ラウロイルパーオキシド、ベンゾイルパーオキシド、*t*-ブチルパーオキシ-2-エチルヘキサノエート、ジ-イソプロピルパーオキシジカーボネート、ジ-*t*-ブチルパーオキシイソフタレート、*t*-ブチルパーオキシイソブチレート等の他の過酸化物類などが例示される。これら重合開始剤と還元剤とを組み合わせたレドックス開始剤を使用することもできる。

【0046】これらのうち、重合性単量体に可溶性油溶性ラジカル開始剤が好ましく、必要に応じて、水溶性の開始剤をこれと併用することもできる。重合開始剤の使用割合は、重合性単量体100重量部に対して、通常0.1～20重量部、好ましくは0.3～15重量部、より好ましくは0.5～10重量部である。この使用割合が小さすぎると重合速度が遅く、大きすぎると分子量が低くなる。重合開始剤は、単量体組成物中に予め添加することができるが、早期重合を避けるなどの目的で、水系分散媒体中での単量体組成物の造粒工程終了後に懸濁液中に添加することもできる。また、重合開始剤の使



用割合は、水系分散媒体基準で、通常0.001～3重量%程度である。

#### 【0047】(11) 分散安定剤

本発明に用いられる分散安定剤としては、硫酸バリウム、硫酸カルシウムなどの硫酸塩；炭酸バリウム、炭酸カルシウム、炭酸マグネシウムなどの炭酸塩；リン酸カルシウムなどのリン酸塩；酸化アルミニウム、酸化チタン等の金属酸化物；水酸化アルミニウム、水酸化マグネシウム、水酸化第二鉄等の金属水酸化物；ポリビニルアルコール、メチルセルロース、ゼラチン等の水溶性高分子；アニオン性界面活性剤、ノニオン性界面活性剤、両性界面活性剤等の界面活性剤；などを挙げることができる。これらのうち、硫酸塩、炭酸塩、金属酸化物、金属水酸化物などの金属化合物が好ましく、難水溶性の金属化合物のコロイドがより好ましい。特に、難水溶性の金属水酸化物のコロイドは、トナー粒子の粒径分布を狭くすることができ、画像の鮮明性が向上するので好適である。

【0048】難水溶性金属化合物のコロイドは、その製法による制限はないが、水溶性多価金属塩化合物の水溶液のpHを7以上に調整することによって得られる難水溶性金属水酸化物のコロイド、特に水溶性多価金属塩化合物と水酸化アルカリ金属との水相中の反応により生成する難水溶性の金属水酸化物のコロイドが好ましい。難水溶性金属化合物のコロイドは、個数粒径分布 $D_{50}$ （個数粒径分布の50%累積値）が0.5 $\mu\text{m}$ 以下で、 $D_{90}$ （個数粒径分布の90%累積値）が1 $\mu\text{m}$ 以下であることが好ましい。コロイドの粒径が大きくなりすぎると、重合の安定性が崩れ、また、トナーの保存性が低下する。

【0049】この分散安定剤は、重合性単量体100重量部に対して、通常0.1～20重量部、好ましくは0.3～10重量部の割合で使用する。この使用割合が少なすぎると、十分な重合安定性を得ることが困難であり、重合凝集物が生成しやすくなる。逆に、この使用割合が多すぎると、微粒子の増加によりトナー粒子の粒径分布が広がったり、水溶液粘度が大きくなって重合安定性が低くなる。

#### 【0050】(12) 着色重合体粒子の製造方法

重合トナーは、分散安定剤を含有する水系分散媒体中で、少なくとも重合性単量体及び着色剤を含有する単量体混合物を懸濁重合することにより、着色重合体粒子として得ることができる。より具体的には、重合性単量体、着色剤、第三級チオール、帯電制御剤、低軟化点物質などを混合し、ビーズミルなどを用いて均一に分散させて、油性の混合液である単量体混合物を調製する。次いで、この単量体混合物を、分散安定剤を含有する水系分散媒体中に投入し、攪拌機で攪拌して、単量体混合物の液滴の粒径が一定になってから、重合開始剤を投入し、単量体混合物の液滴中に移行させる。次に、高剪断

力を有する混合装置を用いて、単量体混合物の液滴をさらに微細な液滴にまで造粒する。このようにして、生成する重合トナーの粒径にほぼ匹敵する程度の粒径を持つ微細な液滴にまで造粒した後、通常、30～200℃の温度で重合する。このようにして、着色重合体粒子を生成させる。生成した着色重合体粒子は、重合トナーとして使用される。

#### 【0051】(2) コア・シェル構造の重合体粒子の製造方法

10 コア・シェル構造の重合トナーは、スプレッドライ法、界面反応法、*in situ* 重合法、相分離法などの方法により製造することができる。特に*in situ* 重合法や相分離法は、製造効率がよく好ましい。*in situ* 重合法では、分散安定剤を含有する水系分散媒体中で、少なくとも重合性単量体及び着色剤を含有する単量体混合物を懸濁重合することにより得られた着色重合体粒子をコアとし、該コアの存在下にシェル用重合性単量体を懸濁重合することにより、コア・シェル構造の重合体粒子（重合トナー）を得ることができる。本発明では、コアとなる着色

20 重合体粒子の製造に際し、単量体混合物中に第三級チオールを含有させる。  
【0052】シェル用重合性単量体を重合反応系に添加する際に、水溶性の重合開始剤を添加すると、コア・シェル型の構造を持つ重合体粒子を生成しやすくなる。水溶性重合開始剤としては、過硫酸カリウム、過硫酸アンモニウム等の過硫酸塩；4, 4'-アゾビス(4-シアノ吉草酸)、2, 2'-アゾビス(2-アミジノプロパン)二塩酸塩、2, 2'-アゾビス-2-メチル-N-1, 1'-ビス(ヒドロキシメチル)-2-ヒドロキシエチルプロピオアミド等のアゾ系開始剤；クメンパーオキシド等の油溶性開始剤とレドックス触媒の組合せ；などを挙げることができる。水溶性重合開始剤の量は、水系分散媒体基準で、通常、0.001～3重量%である。

30 【0053】シェル用重合性単量体として、コアの着色重合体粒子を構成する重合体成分のガラス転移温度よりも高いガラス転移温度の重合体を生成することができる重合性単量体を使用することにより、重合トナーの耐ブロッキング性、即ち、保存性を高めることができる。コア用重合性単量体としては、ガラス転移温度が、通常60℃以下、好ましくは40～60℃程度の重合体を生成し得るものが好適である。シェル用重合性単量体としては、コアを形成する重合体成分のガラス転移温度より10℃以上、好ましくは20℃以上、より好ましくは30℃以上高いガラス転移温度の重合体を生成し得るものが好適である。シェル用重合性単量体から形成される重合体のガラス転移温度は、通常、50℃超過120℃以下、好ましくは60℃超過110℃以下、より好ましくは80～105℃である。なお、ガラス転移温度は、各単量体の種類と使用割合から、常法に従って計算により

算出される値である。

【0054】コア用重合性単量体とシェル用重合性単量体は、通常、80:20~99.9:0.1の重量比で使用される。シェル用重合性単量体の割合が過小であると、保存性改善効果が小さく、逆に、過大であると、定着温度の低減の改善効果が小さくなる。シェルの厚みは、通常、0.001~1.0 $\mu$ m、好ましくは0.003~0.5 $\mu$ m、より好ましくは0.005~0.2 $\mu$ mである。

#### 【0055】2. 静電荷像現像用トナー

本発明の静電荷像現像用トナーは、好ましくは、前述の重合法により得ることができる。本発明の製造方法により得られる重合トナー（コア・シェル構造の重合トナーを含む）は、体積平均粒径（ $d_v$ ）が、通常1~12 $\mu$ m、好ましくは2~11 $\mu$ m、より好ましくは3~10 $\mu$ mである。特に高精細な画像を得る用途に使用する場合には、重合トナーの体積平均粒径を好ましくは2~9 $\mu$ m、より好ましくは3~8 $\mu$ mにまで小さくすることができる。本発明の製造方法により得られる重合トナーの粒径分布＝体積平均粒径（ $d_v$ ）／個数平均粒径（ $d_p$ ）は、通常、1.7以下、好ましくは1.5以下、より好ましくは1.3以下である。重合トナーの体積平均粒径及び粒径分布を前記範囲内に調整することにより、解像度を高めることができる。

【0056】本発明の静電荷像現像用トナーの結着樹脂は、その合成時に、連鎖移動剤として第三級チオールが用いられているため、該第三級チオールの連鎖移動反応に起因するアルキルチオ基が結合した重合体である。アルキルチオ基は、少なくとも2個の第三級炭素原子を有し、かつ、そのうちの少なくとも1個の第三級炭素原子には硫黄原子が直接結合した構造を持つ炭素原子数7~20のアルキルチオ基である。アルキルチオ基の結合位置は、特に制限されないが、第三級チオールの連鎖移動の機序からみて、通常、重合体の分子鎖末端である。

【0057】本発明の製造方法により得られた重合トナーは、必要に応じて、流動性や研磨性などの向上を目的として、汎用の外添剤と混合して用いることができる。外添剤としては、無機粒子及び／または有機樹脂粒子が挙げられる。無機粒子としては、二酸化ケイ素、酸化アルミニウム、酸化チタン、酸化亜鉛、酸化錫、チタン酸バリウム、チタン酸ストロンチウム等が挙げられる。有機樹脂粒子としては、メタクリル酸エステル重合体粒子、アクリル酸エステル重合体粒子、スチレン-メタクリル酸エステル共重合体粒子、スチレン-アクリル酸エステル共重合体粒子、ステアリン酸亜鉛、ステアリン酸カルシウム、コアがメタクリル酸エステル共重合体でシェルがスチレン重合体で形成されたコアシェル型粒子等が挙げられる。これらのうち、無機酸化物粒子、特に二酸化ケイ素粒子が好適である。これらの粒子の表面を疎水化処理することができ、疎水化処理された二酸化ケイ

素粒子が特に好適である。外添剤の量は、特に限定されないが、重合トナー100重量部に対して、通常、0.1~6重量部である。

【0058】外添剤は2種以上を組み合わせ用いてもよい。外添剤を組み合わせ用いる場合には、平均粒径の異なる無機粒子同士または無機粒子と有機樹脂粒子を組み合わせる方法が好適である。外添剤の付着は、通常、外添剤と重合トナーとをヘンシェルミキサーなどの混合機に入れて攪拌して行う。

10 【0059】本発明の静電荷像現像用トナー（外添剤を含有するものを含む）は、フローテスターで測定したトナーの軟化点（ $T_s$ ）が62~67℃で、流出開始点（ $T_{fb}$ ）が110℃以上であることが好ましい。フローテスターを用いて、トナー試料を一定の昇温速度で加熱しながら、プランジャーに一定荷重を与えて、ノズルから押し出すようにし、これによって、フローテスターのプランジャーの降下量-温度曲線を描く（温度目盛りが横軸）。この曲線の最初の立ち上がり時点での高さを軟化点（軟化し、内部空隙が消失した温度； $T_s$ ）と呼ぶ。さらに加熱すると、曲線が急傾斜で立ち上がるが、その時点を出発点（溶融したトナーがノズルから流れ出す温度； $T_{fb}$ ）と呼ぶ。フローテスターを用いた溶融特性の測定法の詳細は、後述する。

20 【0060】トナーの軟化点（ $T_s$ ）温度が低いほど、低温定着性に優れ、流出開始点（ $T_{fb}$ ）温度が高いほど、オフセット発生温度が高くなり、オフセットが発生しにくくなる。軟化点（ $T_s$ ）温度が低くても、流出開始点（ $T_{fb}$ ）温度も低い場合は、オフセットが発生しやすくなる。フローテスターで測定したトナーの軟化点（ $T_s$ ）は、63~66℃の範囲がより好ましく、流出開始点（ $T_{fb}$ ）は、120℃以上であることがより好ましく、130℃以上であることが特に好ましい。連鎖移動剤として、前記特定の第三級チオールを用いることにより、トナーにこれらの望ましい溶融特性を与えることができる。

30 【0061】本発明の静電荷像現像用トナー（特にコア・シェル構造の重合トナー）を用いると、定着温度を好ましくは80~160℃、より好ましくは100~140℃程度の温度に低減することができ、しかもオフセット発生温度を200℃以上の高温に維持することができる。本発明の静電荷像現像用トナーは、保存性と流動性に優れ、印字時に刺激臭の発生がなく、高解像度で良好な画質の画像を形成することができる。

#### 【0062】

【実施例】以下に実施例及び比較例を挙げて、本発明をより具体的に説明するが、本発明は、これらの実施例のみに限定されるものではない。なお、部及び%は、特に断りのない限り重量基準である。実施例及び比較例における物性の測定方法は、以下のとおりである。

50 【0063】（1）粒径及び粒径分布

重合体粒子の体積平均粒径 ( $d_v$ ) 及び粒径分布〔体積平均粒径 ( $d_v$ ) / 個数平均粒径 ( $d_n$ )〕は、マルチサイザー (ベックマン・コールター社製) により測定した。このマルチサイザーによる測定は、アパーチャー径 = 100  $\mu\text{m}$ 、媒体 = イソトンII、濃度 = 10%、測定粒子個数 = 100, 000個の条件で行った。 \*

$$x = r (1 + s / 100 \rho)^{1/3} - r$$

ただし、

$r$  : シェル用単量体の添加前のコア重合体粒子の平均粒径 (マルチサイザーの体積粒径 :  $\mu\text{m}$ ) の半径

$x$  : シェル厚み ( $\mu\text{m}$ )

$s$  : シェル用単量体の添加部数 (コア用単量体100部に対する部数)

$\rho$  : シェル重合体の密度 ( $\text{g}/\text{cm}^3$ ) ; 通常  $\rho = 1.0$  として算定。

#### 【0065】(3) 溶解特性

高化式フローテスター (島津製作所製、CFT-500C) を用い、下記の測定条件で常法に従ってブランジャー降下量-温度曲線を作成し、トナーの軟化点 ( $T_s$ ) 及び流出開始点 ( $T_{fb}$ ) の各温度を求めた。

開始温度 : 35.0  $^{\circ}\text{C}$ 、

到達温度 : 250.0  $^{\circ}\text{C}$ 、

測定間隔 : 2.5  $^{\circ}\text{C}/\text{毎}$ 、

昇温速度 : 3.0  $^{\circ}\text{C}/\text{min}$ 、

予熱時間 : 300 sec、

試験荷重 : 10.0  $\text{kgf}/\text{cm}^2$ 、

ノズル穴径 : 0.50 mm、

ノズル長さ : 1.00 mm、

ピストン : 1.0  $\text{cm}^3$ 。

#### 【0066】(4) 印字試験

温度23  $^{\circ}\text{C}$ 、相対湿度50%の条件で、市販の非磁性一成分現像方式のプリンター (印字速度 = 16枚/分) を用いて、このプリンターの現像装置に評価する重合トナーを入れ、初期から連続印字を行い、反射濃度計 (マクベス製) で印字濃度 (初期印字濃度) を測定した。また、2万枚の連続印字後、白色度計 (日本電色製) で非画像部の感光体上のカブリを調べた。カブリは、感光体上の非画像部に粘着テープ (住友スリーエム社製スコッチメンディングテープ810-3-18) を付着させて調べた。具体的には、印字前の感光体の非画像部に粘着テープを付着させてから剥し、これを印字用紙に貼り付けて、白色度Aを測定する。一方、印字後の感光体の非画像部に粘着テープを付着させてから剥し、これを印字用紙に貼り付けて、白色度Bを測定する。カブリ (%) は、 $A - B$ により算出することができる。連続印字は、5%印字濃度で行った。

#### 【0067】(5) 定着温度

市販の非磁性一成分現像方式のプリンター (印字速度 = 16枚/分) の定着ロール部の温度を変化できるように改造したプリンターを用いて、定着試験を行った。定着

#### \*【0064】(2) シェル厚み

コア・シェル構造の重合トナーのシェルの厚みは、厚ければ、マルチサイザーや電子顕微鏡で測定が可能であるが、実施例及び比較例のように薄い場合には、以下の式を用いて算出する。

$$(1)$$

試験は、改造プリンターの定着ロールの温度を変化させて、それぞれの温度での現像剤の定着率を測定し、温度-定着率の関係を求めることにより行った。定着率は、温度を変化させたとき定着ロールの温度を安定化させるため5分間以上放置し、その後改造プリンターで印刷した試験用紙における黒ベタ領域の、テープ剥離操作前後の画像濃度の比率から計算した。すなわち、テープ剥離前の画像濃度をID前、テープ剥離後の画像濃度をID後とすると、定着率は、次式から算出することができる。

$$\text{定着率}(\%) = (\text{ID後} / \text{ID前}) \times 100$$

ここで、テープ剥離操作とは、試験用紙の測定部分に粘着テープ (住友スリーエム社製スコッチメンディングテープ810-3-18) を貼り、一定圧力で押圧して付着させ、その後、一定速度で紙に沿った方向に粘着テープを剥離する一連の操作である。また、画像濃度は、マクベス社製反射式画像濃度測定機を用いて測定した。この定着試験において、定着率80%に該当する定着ロール温度を現像剤の定着温度とした。

#### 【0068】(6) ホットオフセット発生温度

定着温度と同様に定着温度を変えて、黒ベタを印字させ、オフセットの発生した時の定着ロール温度をホットオフセット発生温度とした。

#### 【0069】(7) 流動性比 (流動性と保存性の評価)

目開きが各々150  $\mu\text{m}$ 、75  $\mu\text{m}$ 、及び45  $\mu\text{m}$ の3種の篩いをこの順に上から重ねて、一番上の篩い上に測定する重合トナー4gを精秤して載せる。次いで、この重ねた3種の篩いを粉体測定機 (細川ミクロン社製、商品名「パウダーテスター」) を用いて、振動強度目盛り4の条件で15秒間振動した後、各篩い上に残った現像剤の重量を測定する。各測定値を以下の式①、②、及び③に入れて、a、b、及びcの値を求め、次に、これらの値を式④に入れて、流動性の値を算出する。1サンプルにつき3回測定し、その平均値を求めた。

$$\textcircled{1} a = [(150 \mu\text{m} \text{ 篩に残った重合体重量}(q)) / 4 \text{ g}] \times 100$$

$$\textcircled{2} b = [(75 \mu\text{m} \text{ 篩に残った重合体重量}(q)) / 4 \text{ g}] \times 100 \times 0.6$$

$$\textcircled{3} c = [(45 \mu\text{m} \text{ 篩に残った重合体重量}(q)) / 4 \text{ g}] \times 100 \times 0.2$$

$$\textcircled{4} \text{流動性}(\%) = 100 - (a + b + c)$$

以上のようにして現像剤の初期の流動性 (F。) を測定する。一方、現像剤を容器に入れて、50  $^{\circ}\text{C}$ で5日間保

存した後、同様にして、流動性 ( $F_1$ ) を測定する。流動性比 ( $F_1/F_0$ ) を算出し、保存性 (耐ブロッキング性) と流動性の指標とした。

#### 【0070】(8) 臭気の評価

前述の印字試験において、印字紙出口付近での臭気を5人の健康人で官能評価し、次の基準で臭気の評価を行った。

- A: 5人が臭気を感じない、  
B: 1~2人が臭気を感じる、  
C: 3人以上が臭気を感じる。

#### 【0071】【実施例1】

##### (1) 単量体組成物の調製

スチレン80.5部及びn-ブチルアクリレート19.5部からなるコア用重合性単量体 (得られる共重合体の計算 $T_g = 55^\circ\text{C}$ )、ポリメタクリル酸エステルマクロモノマー (東亜合成化学工業社製、商品名「AA6」、 $T_g = 94^\circ\text{C}$ ) 0.3部、ジビニルベンゼン (工業用純度55%) 0.6部、2, 2, 4, 6, 6-ペンタメチルヘプタン-4-チオール1.0部、カーボンブラック (三菱化学社製、商品名「#25B」) 7.0部、帯電制御剤 (保土ヶ谷化学社製、商品名スピロンブラックTRH) 1.0部、離型剤 (シェル・MDS社製、商品名「FT-100」) 2部を通常の攪拌装置で攪拌、混合した後、メディア型分散機により、均一分散した。

##### 【0072】(2) 水系分散媒体の調製

室温でイオン交換水250部に塩化マグネシウム (水溶性多価金属塩) 10.2部を溶解した水溶液に、イオン交換水50部に水酸化ナトリウム (水酸化アルカリ金属) 6.2部を溶解した水溶液を攪拌下で徐々に添加して、水酸化マグネシウムコロイド (難水溶性の金属水酸化コロイド) 分散液を調製した。生成した上記コロイドの粒径分布をマイクロトラック粒径分布測定器 (日機装社製) で測定したところ、粒径は、 $D_{50}$  (個数粒径分布の50%累積値) が $0.35\mu\text{m}$ で、 $D_{90}$  (個数粒径分布の90%累積値) が $0.84\mu\text{m}$ であった。このマイクロトラック粒径分布測定器による測定においては、測定レンジ=0.12~704 $\mu\text{m}$ 、測定時間=30秒、媒体=イオン交換水の条件で行った。

##### 【0073】(3) シェル用重合性単量体の調製

メチルメタクリレート (計算 $T_g = 105^\circ\text{C}$ ) 3部と水100部を超音波乳化機にて微分散化処理して、シェル用重合性単量体の水分散液を得た。水分散液中のシェル用重合性単量体の液滴の粒径は、得られた液滴を1%ヘキサメタリン酸ナトリウム水溶液中に濃度3%で加え、マイクロトラック粒径分布測定器で測定したところ、 $D_{50}$ が $1.6\mu\text{m}$ であった。

##### 【0074】(4) 造粒工程

上記(2)で得られた水酸化マグネシウムコロイド分散液に、室温で、上記(1)で得られた単量体混合物を投入し、液滴が安定するまで攪拌し、そこに重合開始剤とし

てn-ブチルパーオキシ-2-エチルヘキサノエート (日本油脂社製、商品名「パーブチルO」) 5部を添加後、エバマイルダー (荏原製作所社製、商品名「MDN303V型」) を用いて15,000rpmの回転数で10分間高剪断攪拌して、単量体混合物の液滴を造粒した。

##### 【0075】(5) 懸濁重合工程

上記(4)で造粒した単量体混合物の水分散液を、攪拌翼を装着した反応器に入れ、 $95^\circ\text{C}$ で重合反応を開始し、重合転化率がほぼ100%に達したときに、サンプリングし、着色重合体粒子 (コア) の粒径を測定した。この結果、コア粒子の体積平均粒径は、 $7.0\mu\text{m}$ であった。次に、前記(3)で調製したシェル用重合性単量体と水溶性開始剤 (和光純薬社製、商品名「VA-086」; 2, 2'-アゾビス [2-メチル-N-(2-ヒドロキシエチル)-プロピオンアミド]) 0.3部を蒸留水65部に溶解し、それを反応器に入れた。8時間重合を継続した後、反応を停止し、 $\text{pH}9.5$ の重合体粒子の水分散液を得た。上記により得た重合体粒子の水分散液を攪拌しながら、硫酸により系の $\text{pH}$ を約5.0にして酸洗浄 ( $25^\circ\text{C}$ 、10分間) を行った。次いで、濾過、脱水し、脱水後、洗浄水を振りかけて水洗浄を行った。その後、乾燥器 ( $45^\circ\text{C}$ ) にて2昼夜乾燥を行い重合体粒子を得た。

##### 【0076】(6) 現像剤

上記(5)で得られたコア・シェル構造の重合体粒子100部に、疎水化処理した平均粒子径14nmのシリカ (デグサ社製; 商品名「R972」) 0.8部を添加し、ヘンシェルミキサーを用いて混合して非磁性一成分現像剤を得た。結果を表1に示す。

【0077】【実施例2】実施例1の(1) 単量体組成物の調製工程において、架橋剤のジビニルベンゼンの添加量を0.6部から0.7部に、また、連鎖移動剤の2, 2, 4, 6, 6-ペンタメチルヘプタン-4-チオールの添加量を1.0部から2.0部に、それぞれ変更したこと以外は、実施例1と同様に実施した。結果を表1に示す。

【0078】【実施例3】実施例1の(1) 単量体組成物の調製工程において、帯電制御剤のスピロンブラックTRHをFCA626N (藤倉化成社製の帯電制御樹脂、 $M_w$ =約27,000、 $M_n$ =約8,000、スルホン酸基付加構造単位比7モル%のスチレン-アクリルエステル樹脂) に変更したこと以外は、実施例1と同様に実施した。結果を表1に示す。

【0079】【実施例4】実施例1の(1) 単量体組成物の調製工程において、帯電制御剤のスピロンブラックTRHをFCA626Nに、また、離型剤の「FT-100」2部をジペンタエリスリトールヘキサミリストート10部に、それぞれ変更したこと以外は、実施例1と同様に実施した。結果を表1に示す。

【0080】【比較例1】実施例1の(1)単量体組成物の調製工程において、連鎖移動剤の2, 2, 4, 6, 6-ペンタメチルヘプタン-4-チオールをt-ドデシルメルカプタンに変更したこと以外は、実施例1と同様に実施した。結果を表1に示す。

【0081】【比較例2】比較例1において、t-ドデ\*

\*シルメルカプタンの添加量を1.0部から2.0部に変更したこと以外は、比較例1と同様に実施した。結果を表1に示す。

【0082】

【表1】

	実 施 例				比 較 例	
	1	2	3	4	1	2
<b>コア (部)</b>						
スチレン	80.5	80.5	80.5	80.5	80.5	80.5
n-BA (*1)	19.5	19.5	19.5	19.5	19.5	19.5
マクロモノマー	0.3	0.3	0.3	0.3	0.3	0.3
架橋剤 (DVB) (*2)	0.6	0.7	0.6	0.6	0.6	0.7
着色剤 (CB) (*3)	7.0	7.0	7.0	7.0	7.0	7.0
帯電制御剤 (*4)	TRH	TRH	FCA	FCA	TRH	TRH
	1.0	1.0	1.0	1.0	1.0	1.0
離型剤 (*5)	FT-100	FT-100	FT-100	DPEHM	FT-100	FT-100
	2.0	2.0	2.0	10.0	2.0	2.0
連鎖移動剤						
PMHT (*6)	1.0	2.0	1.0	1.0	-	-
TDM (*7)	-	-	-	-	1.0	2.0
<b>シェル (部)</b>						
MMA (*8)	3.0	3.0	3.0	3.0	3.0	3.0
<b>重合トナー</b>						
体積平均粒径 (dv)	7.1	7.1	7.2	7.1	7.2	7.1
粒径分布 (dv/dn)	1.20	1.20	1.19	1.21	1.20	1.21
シェル厚 (μm)	0.04	0.04	0.04	0.04	0.04	0.04
溶融特性						
Ts (°C) (*9)	63.4	64.0	65.1	64.5	62.7	60.5
Tfb (°C) (*10)	132	148	138	135	125	110
<b>現像剤特性</b>						
印字濃度	1.42	1.45	1.43	1.45	1.43	1.45
2万枚印字後						
カブリ	1.2	0.8	1.3	1.5	1.5	1.4
定着温度 (°C)	135	135	140	125	165	130
ホットオフセット						
発生温度 (°C)	220	220	220	220	220	150
保存 (50°C/5日) 前						
後の流動性比	0.98	0.95	1.16	0.99	0.97	0.35
印字臭気	A	A	A	A	B	C

【0083】(脚注)

(\*1)n-BA: n-ブチルアクリレート

(\*2)DVB: ジビニルベンゼン (純度55%)

(\*3)CB: カーボンブラック

(\*4)帯電制御剤

TRH: 保土ヶ谷化学社製、スピロンブラックTRH

FCA: 藤倉化成社製、帯電制御樹脂FCA626N

(\*5)離型剤

FT-100: シェル・MDS社製、フィッシュアトロブシュワックス

DPEHM: ジベンタエリスリトールヘキサミリスター

(\*6)PMHT: 2, 2, 4, 6, 6-ペンタメチルヘプタン-4-チオール

(\*7)TDM: t-ドデシルメルカプタン

(\*8)MMA: メチルメタクリレート

(\*9)Ts: トナーの軟化点

(\*10)Tfb: トナーの流出開始点

【0084】表1の結果から明らかなように、連鎖移動剤として特定の第三級チオールを用いることにより(実施例1~4)、定着温度を低減させ、しかもなお、オフセット温度を高温に維持し、臭気がなく、高画質の画像を形成することができる静電荷像現像用トナーを得ることができる。これに対して、汎用の連鎖移動剤であるt-ドデシルメルカプタンを用いると、その添加量が少ない場合(比較例1)には定着温度を下げることができず、添加量が多い場合(比較例2)には、定着温度を低下させることができるものの、オフセット温度が著しく低下し、しかも印字時の臭気がひどくなり、保存性も低下する。

【0085】

50 【発明の効果】本発明によれば、定着温度が低く、省エ

エネルギー化、印字及び複写の高速化、カラー化などに対応することができ、しかも保存性と流動性に優れ、オフセット温度が高く、臭気の発生もなく、高解像度で良好な画質の画像を形成することが可能な静電荷像現像用ト

ナーが提供される。本発明の静電荷像現像用トナーは、電子写真法、静電印刷法、静電記録法などにおいて、静電潜像を現像するための現像剤として各種画像形成装置で使用する事ができる。